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ORGANOSILICON COMPOUNDS AS POTENTIAL WOOD PROTECTING AGENTS

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Liesbeth Lochristi, 31 juli 2009

SAMENVATTING

Hout is een uniek materiaal dat door zijn grote verscheidenheid aan eigenschappen zowel voor binnen- als voor buitentoepassingen geschikt is. Elk gebruik vereist echter specifieke bescherming om een zo lang mogelijke levensduur te kunnen garanderen. Producenten van houten componenten zijn dan ook steeds op zoek naar verbeterde of nieuwe behandelingsmethodes die zo doeltreffend en kostenefficiënt mogelijk zijn. Gezien de toenemende druk vanuit onze hedendaagse maatschappij op gezondheids- en milieugerelateerde aspecten, wordt langzaamaan afgestapt van biociden als houtbeschermingsmiddelen. Als alternatief kan hout gemodificeerd worden of behandeld met organische siliciumverbindingen, wat in dit werk verder werd onderzocht. Om na te gaan of deze behandelingen voldoende efficiënt zijn moeten meerdere parameters geëvalueerd worden.

Eerst werd dieper ingegaan op methodes ter lokalisatie van organische siliciumverbindingen in hout. Dit heeft als doel na te gaan waar de producten zich exact bevinden en inzicht te verwerven in hun werking. De scanning methodes die in deze thesis zijn gebruikt blijken geschikt voor dat doel. Gezien de steeds snellere ontwikkelingen in het domein van de scanning technieken, mag verwacht worden dat deze methodes nog nauwkeuriger en toegankelijker zullen worden in de toekomst. Behalve lokalisatie werd ook een validatie gedaan van een methode ter bepaling van de hoeveelheid aangebracht product. Deze methode zou toelaten om kwaliteitscontroles uit te voeren, zowel gedurende het productieproces als op de werf. De resultaten hebben echter aangetoond dat meer onderzoek nodig is om de techniek verder op punt te stellen.

Zowel voor de producent als consument is het belangrijk te kunnen vertrouwen op het behandelde hout. In eerste instantie is er de bescherming van hout tegen houtrot veroorzaakt door bepaalde schimmels. Behalve de doeltreffendheid tegen aantasting werden ook verschillende evaluatiemethodes zelf geverifieerd.

Hieruit bleek dat aanpassingen nodig zijn om de waarde van organische siliciumverbindingen als houtbeschermende producten goed te kunnen schatten. Omdat, zoals eerder aangehaald, ook milieugerelateerde aspecten belangrijk zijn, werd onderzoek verricht naar de toxiciteit van het uitloogwater van behandeld hout. Een terugkoppeling naar de werkzaamheid van de behandelingen leerde dat het niet steeds eenvoudig is voldoende bescherming tegen houtaantastende schimmels te bieden zonder het milieu extra te belasten.

Behalve bescherming tegen schimmels wordt hout ook best behandeld tegen vochtopname. Dit vocht zorgt er namelijk voor dat verscheidene houteigenschappen wijzigen en dat het hout ook vatbaarder wordt voor schimmelaantastingen. Aangezien organische siliciumverbindingen al lang gekend zijn als waterafstotende producten op onder andere textiel en cementhoudende producten, werd verondersteld dat zij ook een positieve invloed op hout konden hebben. Dit onderzoek heeft echter aangetoond dat onder laboratoriumomstandigheden geen significante invloed van de organische siliciumverbindingen mag verwacht worden. Hoopgevendere resultaten werden gevonden wanneer grotere houten elementen werden behandeld. Deze onderdelen werden buiten geplaatst en aldus blootgesteld aan natuurlijke verwering. Na meerdere jaren expositie kon vastgesteld worden dat zowel de oppervlakkige schimmelaantasting, het houtvochtgehalte als het massaverlies kleiner waren door de behandelingen. Deze resultaten tonen dus aan dat de verbindingen onder realistische omstandigheden beter presteren dan onder extreme situaties, zoals in laboratoriumproeven vaak het geval is.

Algemeen kan dus gesteld worden dat organische siliciumverbindingen slechts een klein potentieel hebben om hout effectief te beschermen tegen allerlei invloeden van buitenaf. Het lijkt dan ook waarschijnlijker dat deze producten toegevoegd worden aan houtbeschermingsmiddelen ter verbetering van de prestaties, dan dat ze als alleenstaand product zullen worden toegepast.

SUMMARY

Wood is very diverse and has specific features making it easily distinguishable from other materials. Due to its properties it can be applied both inside and outside, making it a rewarding material to work with. However, when applied outside it is liable to weathering, inducing changes to the wood, like i.e. surface discolouration, dimensional changes or even wood rot, which are not appreciated by end-users. Therefore wood constructors are looking for protection methods of wood, leading to longer service life of their wood products.

Since pressure is put on traditional wood preservation due to environmental and health considerations, new treatment technologies aiming at improved wood properties are launched. Besides wood modification technologies, treatments with organosilicon compounds were proposed. These chemicals proved to be suitable for the protection of other building materials like concrete and might therefore also be suited for wood.

To be able to optimise the treatment process and perform quality control afterwards, detection techniques of organosilicons in treated wood could be very helpful. Visualisation combining several scanning techniques proved to be suitable for this purpose and with new, more precise technologies being developed, the possibilities will only grow. However, before quantitative determination will be useful for these purposes obstacles related to the accuracy of the chemical analysis need to be overcome.

Since fungal attack is of major concern for the performance of a specific element, research was done to determine the fungal resistance of organosilicon treated wood and on methodology how to properly interpret the results. Furthermore care must be taken with the ecotoxicological consequences of the applied products. Therefore a study was devoted to developing a methodology determining on one hand the fungal efficacy of a certain treatment, while on the

other hand the impact to the environment of this treatment was estimated. It was found that improving one parameter was often at the expense of the other parameter. Addition of a biocide improved fungal resistance, but increased the ecotoxicological risk of the leachates of the treated wood.

Organosilicons are known as water repellents and are assumed to interfere in the wood-water relationship. Whatever laboratory test performed, this assumption could not be corroborated when organosilicons were applied at concentrations supposed to be economically feasible. When evaluating high retentions to the envelope of the material, better performance was achieved and this both for solid wood and plywood. However, the efficacy was reduced due to weathering.

It can be stated that none of the laboratory tests was very hopeful for the application of organosilicons at economically feasible concentrations for wood used outdoors, out of ground contact. It was also demonstrated several times that the standard evaluation methods available are not really suitable for the evaluation of newly developed wood treatments. Therefore small-scaled wooden elements were constructed and exposed to accelerated natural weathering. This time organosilicon impregnated wood behaved much better than the untreated Scots pine sapwood reference material. Due to the treatment fungal discolouration, mass loss and moisture content could be reduced, without the application of a biocide. Further adding a biocide enhanced the first two parameters.

Concluding it can be said that organosilicons seem to have certain potential in improving wood characteristics like moisture balance and fungal resistance, as shown in field experiments. Nevertheless it remains doubtful whether that will be sufficient to protect wood in the long term. It is more likely that organosilicons will become one of the components in a more complex formulation than that they will be applied on their own.

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LIST OF ABBREVIATIONS AND ACRONYMS

ΔE	Colour change
2D	Two-dimensional
3D	Three-dimensional
A	Surface area
ai	Active ingredient
ai_conc	Active ingredient concentration
ANOVA	Analysis of Variance
ASE	Anti swelling effectiveness
AsE	Anti shrinkage effectiveness
A_w	Water absorption coefficient
C	Correction value
CCA	Salts of chromium, copper and arsenic
Conc_active_ingr	Concentration of active ingredient
D	Dipping
DC	Durability class
DMDHEU	Dimethylol dihydroxy ethylene urea
DVS	Dynamic vapour sorption
Do	Douglas fir heartwood
D_w	Moisture-liquid diffusivity
EC_{50}	50 % effect concentration
EDX	Energy dispersive X-ray spectrometer
FA	Furfuryl alcohol
Gk	Scots pine heartwood
HDO	(bis[N-cyclohexyldiazeniumdioxy]copper
I	Impregnation
IPBC	3-iodo-2-propynyl-butyl carbamate
La	Larch heartwood
LCA	Life cycle analysis
MC	Moisture content

MDF	Medium density fibreboard
Micro-CT	X-ray Micro-computed tomography
ML	Mass loss
MTES	Methyltriethoxysilane
MTM	Methyltrimethoxysilane
Nano-CT	X-ray Nano-computed tomography
n-OTES	n-octyltriethoxysilane
OSB	Oriented strand board
PAM	Partitioning around mediods
(P)DMS	(poly)dimethylsiloxane
Propiconazole	(±)-(cis+trans)-1-(2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl-methyl)-1H-1,2,4-triazole
PTEO	Propyltriethoxysilane
PTMS	[γ-(methacryloxy)propyl]trimethoxysilane
R × T × L	Radial × Tangential × Longitudinal
R^2	R square
RH	Relative humidity
RWU	Relative water uptake
SEM	Scanning electron microscopy
S	Volumetric swelling
Si-Quat	3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride
SYP	Southern yellow pine
TEOS	tetraethoxysilane
TUs	Toxic units
UV	Ultra-violet light
VTMS	Vinyl trimethoxysilane
w_c	Capillary saturated volumetric moisture content
WPG	Weight percent gain
WRE	Water repellent effectiveness
Wt %	Weight percent
Z	Untreated Scots pine sapwood

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INTRODUCTION

1 INTRODUCTION

1.1 Objectives and outline

Since mankind has come into existence trees have always been on hand. It is therefore not surprising men soon discovered that wood coming from those trees could serve in many ways. The use of wood kept on growing and men started to exploit forests intensively, making the wood become more scarce and valuable. Because of this scarceness and increasing end uses the need for optimal and rational use of wood has evolved. Moreover each of these end uses poses certain minimum criteria to the wood concerning stability, dimensions, durability, aesthetics, etc.

When wood is being used outdoors, out of ground contact, under the so-called use class 3 conditions (EN 335-1 2006), it is exposed to weathering and therefore susceptible to the impact of rain, frost, sunlight, etc. Each of these induces certain changes to wood, possibly leading to degradation. To avoid this degradation, men have searched for alternatives. This can be in other materials like aluminium, brick, concrete, plastics but also wood itself can guarantee a long service-life. In this quest for long-lasting products composite materials based on wood have found their place. But also tropical wood species offer interesting properties like stability and durability. Drawbacks however are i.e. the risk of overexploiting vulnerable habitats and the economic and environmental transportation costs of wood from its region of origin to the region of manufacturing or utilisation.

Another option to protect wood is wood preservation. This means that wood is treated (superficially or in depth) with a product which is toxic to disfiguring or degrading organisms like stains, moulds and wood rotting fungi. One of the most used broad spectrum products for this purpose is CCA (salts of chromium,

copper and arsenic). These products have however a lot of environmental drawbacks and are therefore strictly regulated.

Besides wood preservation also wood modification is a way to protect wood by modifying or changing it in such way that the wood constituents become unreachable or unrecognisable to micro-organisms (Hill 2006). This can be done on the one hand by filling the lumen or the cell wall of wood or on the other hand by changing the chemical structure of wood through binding a chemical to the OH-groups (and possibly further cross-linking them) or changing the wood structure itself (Weigenand 2006). Possible further options are impregnation with oils or resins, filling the lumen of the wood. Several chemicals like acetic anhydride, epoxides, aldehydes, furfuryl alcohol, dimethylol dihydroxy ethylene urea (DMDHEU) are components used to modify the wood structure and consequently the properties. Furthermore there are also thermal and surface modification methods.

As often the case a discovery in one branch is an inspiration for scientists in another branch. The protection of mineral materials like bricks and concrete with organosilicons has not stayed unremarked by wood technologists. The organosilicons and mainly (alkylalkoxy)silanes and (alkylalkoxy)siloxanes have proven to function as water repellents on masonry (Mayer 1998). Making wood more water repellent could lead to better performance of the wood since water and/or moisture is what makes wood swell and shrink and is for most micro-organisms essential to survive. It is therefore not surprising that different researchers have started to define the potential that organosilicons might have in wood protection. Some of these research projects were very promising, while others contradicted this. A lot seemed to depend on the concentration at which the products were applied and the purpose of the treatment.

Therefore several research groups and industrial partners decided to work together in an attempt to develop non-fungicidal (environmentally friendly) silicon-based hydrophobisation agents and methods to protect wood-based

materials against deterioration by micro-organisms and weather conditions. This consortium was able to cooperate during four years in the European research project “Improvement of wood product properties by increased hydrophobicity obtained by the use of silicon compounds”, having the acronym HYDROPHOB (QLK5-CT-2002-01439).

A first dissertation on this subject was written by S. Donath (2004), focussing on the use of silanes. Since he was able to show certain potentials of silanes when used at high concentrations, the use of organosilicons was broadened by O. Weigenand (2006), still operating at relatively high concentrations. Furthermore P. Tingaut (2006) did more fundamental work on the chemistry between wood constituents and organosilicons. Athough each of these dissertations has its own scientific value; none of them investigated the potential of organosilicons under realistic commercial applications. This is however a very important issue that needs to be evaluated before a product can be commercialised.

Underlying dissertation was initiated in the frame of the HYDROPHOB-project. The objective was to investigate whether organosilicons as a group of chemicals can protect wood exposed under use class 3 conditions, when applied at economically feasible concentrations. This general aim was further divided into three specific objectives, corresponding each to a part presented in this work. The chapters mentioned make reference to scientific papers published or at least prepared for publication.

- Part 1: The first specific objective is to try to find a method to localize organosilicons inside wood once treated.
    - Chapter 2: investigation of the possibilities of combining SEM-EDX and micro-CT in detection of silicon inside wood
    - Chapter 3: validation of analytical method for determining the silicon content inside wood

- Part 2: The second objective deals with the influence organosilicons have on the protective capacity of wood against wood rotting fungi. Recalling that the use class envisaged is outdoor performance out of ground contact, wood degradation is an essential parameter in evaluating the suitability of a product group.
    - Chapter 4: determination of decay resistance and durability of organosilicon treated wood
    - Chapter 5: elaborating on methodology combining efficacy and ecotoxicity of preservative treated and modified wood
    - Chapter 6: evaluation of the potential contribution of organosilicons in reducing the leaching of biocides

- Part 3: The last objective looks into the wood-water relationship and outdoor field performance of organosilicon treated wood. It seems logic that a water repellent has a certain influence on the wood-water relationship, but the exact ambit needed further investigation.
    - Chapter 7: a study on moisture related aspects of organosilicon treated solid wood
    - Chapter 8: examination of the influence of highly concentrated organosilicon envelope treatments of wood-based materials
    - Chapter 9: prevention of organosilicon treatments against disfigurement of wood under laboratory and outdoor conditions
    - Chapter 10: illustration of accelerated L-joint outdoor performance of organosilicon treated wood

This thesis is divided into several chapters which can be considered isolated issues and can be read in that way. However, since the same organosilicons (and biocides) are used in most of the chapters and to avoid redundancy in those chapters, a separate part describing the organosilicons and biocides and their application techniques is given in section 1.3. This section should therefore be seen as an essential part of Chapters 4 up to 10, except for Chapter 5.

1.2 Structures and properties

In this section a short overview is given of silicon containing compounds, going from inorganic to organic molecules.

1.2.1 Silicates

A silicate is a compound containing an anion in which one or more central silicon atoms are surrounded by electronegative ligands, usually oxygen. The negative net electrical charge is balanced by a positively charged cation. Silica is a special case of a silicate since there is no negative charge and thus no need for counter-ions. It is found in nature as the mineral quartz. For minerals the basic chemical unit is the SiO_4 tetrahedron anionic group with a negative four charge. The central silicon atom has a charge of positive four while each oxygen has a charge of negative two and thus each Si-O bond is equal to one half the total bond energy of oxygen. This condition leads to three distinct types of mineral silicates: (1) silicates with discrete negatively charged silicon ions (2) silicates with infinite chains of tetrahedra, each sharing two corners with the outside oxygen atoms bearing negative charges and (3) silicates in which the tetrahedra share three corners, leading to flat sheets of alternate silicon and oxygen atoms (such as in clays and micas) (Rochow 1987). Industrially there are a lot of silicates due to many combinations of metal arrangement within the silicate structure (Donath 2004). Water glass is the common name for sodium metasilicate. More general water glasses are solidified gels of silicates (Donath 2004) and mainly based on sodium or potassium silicates. They are colourless, glassy or jellylike substances that dissolve in water at elevated temperatures and pressures (Mai and Militz 2004a). Due to their high pH (>12) silicic acid can be precipitated by acidic solutions. This neutralization reaction can happen with naturally present acids or metal solutions (Mai and Militz 2004a). Without this neutralization they stay alkaline and hygroscopic. This precipitated silicic acid can be heated and roasted to form silica gel, a substance that absorbs moisture. Water glasses dissolved in water are used to preserve eggs and fireproofing porous materials such as cloth, paper and wood. It is also used as

an adhesive for paper and cardboard, binding agent in paints, coating material for building protection, sealing, etc. (Mai and Militz 2004a).

1.2.2 Silanes

Silane is a gas at room temperature and has the chemical formula SiH_4. It undergoes spontaneous combustion in air and above 420 °C it decomposes into silicon and hydrogen. More generally a silane is any compound with the general formula Si_nH_{2n+2}. Polysilanes are not very stable since their Si-Si bonds are not so strong. Oxygen decomposes silanes easily, because the Si-O bond is much stronger.

Silanes containing an organic group are called organosilanes. They have multiple applications like water repellents, masonry protection, anti-graffiti agent, reducing agent in organic and organometallic industry,etc. They are also used as coupling agents to adhere glass fibers to a polymer matrix, thereby stabilizing the material. Another application is as hydrophobing agent against liquid water and/or oleophobation, for example on concrete, by leaving the material open to moisture exchange (Chandra 1997; Donath 2004).

Organosilanes bearing at least one alkoxy group (OR) are called alkoxysilanes. In the presence of water hydrolysis will take place and silanol groups will be formed. These hydroxyl groups can further react and condense, with generation of water which is used in the hydrolysis. Since the condensation reaction starts while hydrolysis is still going on intermediate oligomeric particles, so-called sols are being formed. These will further crosslink and form highly condensed gels. This process is called the sol-gel process and is schematically represented in Figure 1.1. Both reactions are never fully completed, so remaining reactive sites can continue to react and this process is called ageing of the gel structure.

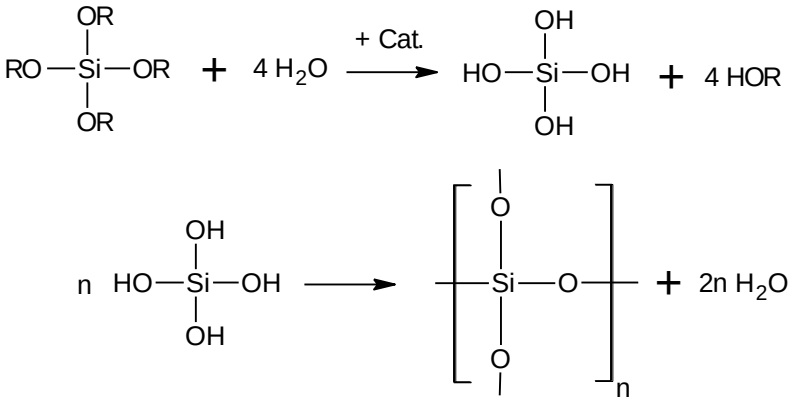


Figure 1.1: Principal reaction of a sol-gel process based on a tetraalkoxysilane (Donath et al. 2004)

Alkyltrialkoxysilanes like n-octyltriethoxysilane (n-OTES) proved to be well adapted for hydrophobation purposes of construction materials. The Si-O bond is sterically protected by the longer alkyl-chains making these products suitable for water repellency of concrete (Roos et al. 2008).

1.2.3 Organosiloxanes – Silicones

Silicon is also a component of silicones, a class-name for various synthetic silicon containing organic compounds. More accurately these polyorganosiloxanes are polymers (Greek *polis* means *many* and *meros* means *parts*) with the basic structure as presented in Figure 1.2.

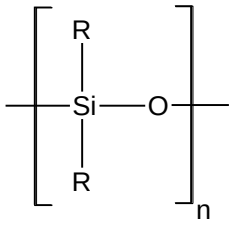


Figure 1.2: Basic structure of silicones

They consist of an inorganic silicon-oxygen backbone with organic side groups (R) attached to the silicon atoms. By varying the –Si-O- chain lengths, side groups, and cross linking, silicones can be synthesized with a wide variety of properties and compositions. There are four main possible functional siloxane units which can be combined (Figure 1.3). Monomeric units (M) serve as chain terminators, while the difunctional units (D) are the chain builders. Trifunctional

units T make the molecules cross-link, whereas quadrifunctional units Q yield three-dimensional cross-linked molecules similar to silicates. The silicones can vary in consistency from liquid to gel to rubber to hard plastic.

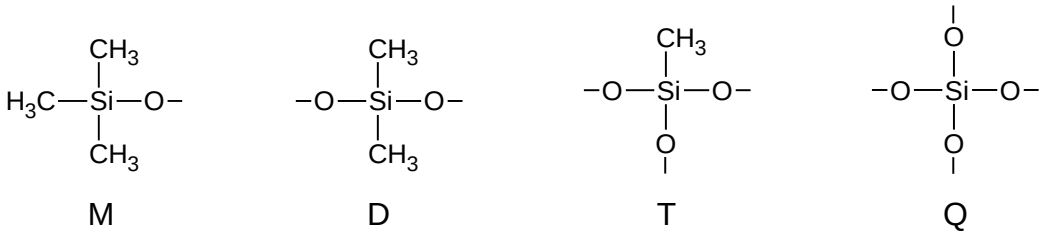


Figure 1.3: Possible functional siloxane monomers

About 80 % of commercial organosilicon polymers is based on polydimethylsiloxanes, which are known for their stability, inertness in the presence of heat, chemicals and UV radiation (Chandra 1997). The most common type is linear polydimethylsiloxane or PDMS. This silicone oil (Figure 1.4) mainly consisting of D units, can be terminated by different M end groups i.e. by methoxy-groups. The linear methylsiloxanes have lower melting points, a much longer liquid range, and lower densities than the cyclic forms. They also have a lower viscosity and change their viscosity more slowly with changing temperature. This makes them suitable as lubricants or hydraulic fluids, insulators, etc. Cyclic siloxanes are widely used in skin care products.

The second largest group of silicone materials is based on silicone resins (Figure 1.4), which are formed by branched and cage-like oligosiloxanes. The most abundant silicone resins are built of D and T units or from M and Q units; however many other combinations are also possible. These highly condensed molecules represent a broad range of products like pressure sensitive adhesives, silicone rubbers, coatings, additives, masonry water repellents, etc (Mayer 1998).

A third group of silicone materials are the elastomers (Figure 1.4). They are mainly built of D units of methyl silicone of extremely high molecular weight and will remain largely independent from one another. However they may

deliberately cross-link at a few selected points at an appropriate time so as to keep the flexible elastic material in place. They are mainly used as rubber, oven seals or for electrical insulation (Rochow 1987; Colas 2005).

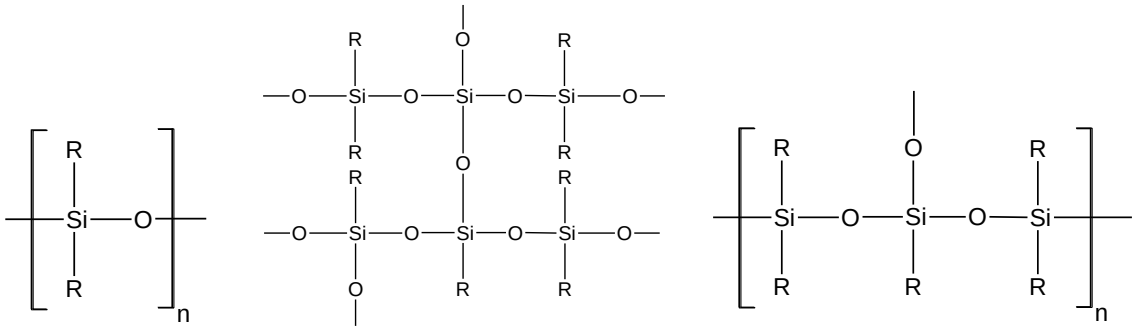


Figure 1.4: Chemical structures of three types of silicones

1.2.4 Macro- and micro-emulsions

In practice usually mixtures of above mentioned molecules are used to protect i.e. masonry or wood. These are traditionally solvent-based, but due to environmental considerations, solvent-free systems are developed. The so-called aqueous emulsions, being a mixture of two immiscible substances, i.e. water and oil, were developed. The products are kept stable by adding an emulsifier. The disadvantages of such macro-emulsions are their tendency toward phase separation upon dilution and an undesirable large droplet size (>1000 nm) with a broad size distribution. The large droplet size and non-uniform size distribution may cause poor penetration of the active ingredient into the wood. The phase separation is even not acceptable for the formulation storage and the treatment process (Yu and Leightley 1993).

Therefore micro-emulsions were developed (Figure 1.5). These emulsions comprise besides molecules to be emulsified (silane, siloxane or polysiloxane) and an emulsifier (silane, siloxane) also an additional component, namely the co-emulsifier (functional polysiloxane). These functional polysiloxanes change during drying into adhesion promoters and catalysts for silicones, thereby becoming inactive. The function of the co-emulsifier is to interfere with the

quasi-crystalline monomolecular surfactant film, thereby making it soft and thus increasing its inclination to bend (Hager 1995). That is why particle sizes from 10 to 80 nm can be reached and this enables them to penetrate into the voids of wood which cannot be reached by conventional emulsions (Mai and Militz 2004b). Since the presence of water starts reaction of the active components in the droplets, dilutions may only be made directly before application. This prohibits the use of such emulsions for pressure or dip treatments on an industrial scale (Lukowsky and Peek 1997). Besides the small droplet size and uniform size distribution consequently leading to an excellent dispersion of the active ingredients, the thermodynamical stability is an advantage of the micro-emulsion.

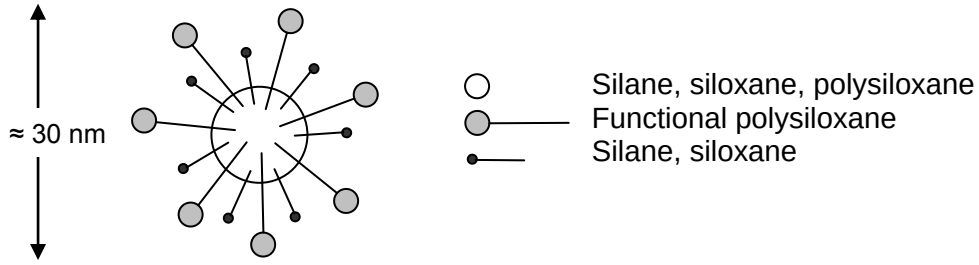


Figure 1.5: Components in a droplet of a micro-emulsion (Hager 1995)

1.3 Materials and methods

1.3.1 Organosilicons and biocides used in this research

Due to an increased awareness of the environmental impact of solvent-based products, more environmentally friendly aqueous solutions are developed by the industry. That is why in this research six water-based products and only two solvent-based products were selected (Table 1.1). All water-based products are emulsions containing the components (poly)dimethylsiloxane (P)DMS and/or (octyl)triethoxysilane (n-O)TES. Also the two solvent-based products contain at least n-OTES.

Table 1.1 gives an overview of all products used and their corresponding main components and active ingredient concentrations. The first product W1 is developed as a water-based wood water repellent, when formulated with a wax emulsion, for applications in use class 3 such as decks, fences, siding, docks etc. It is a milky-white nonionic organosilicone emulsion with 50 % solids content that can be applied by brushing, dipping or low-pressure spraying. Together with a wax emulsion it provides water exclusion, dimensional stability and water beading to the wood, leading to reduced warping and cracking.

The second product W2 is a 40 % active water-dilutable silane/siloxane emulsion which is used as active component for formulating penetrating water repellent treatments on mineral substrates like brick, stone, concrete and mortar. It can be sprayed, rolled or brushed onto the surfaces as supplied or diluted up to 5 % active solid content. The substrates' appearance is not changed after application.

The third water-based product W3 is also a milky-white, nonionic siloxane emulsion. The active content amounts to 60 % and the macro-emulsion can be applied by padding or spraying, most often at very low concentrations. It is designed to impart water repellency on most non-woven substrates. Product W4 is a solventless silicone micro-emulsion based on silanes and siloxanes developed as water repellent for impregnating and priming normal and reinforced concrete. It is usually applied with a low-pressure airless spray.

The water-based organosilicon W5 is a hydroxy end-blocked dimethyl silicone fluid. This milky-white nonionic polydimethylsiloxane has a silicone content of 60 % and is applied in low concentrations either by spraying or dipping as a mould release agent in numerous industrial and specialty chemical applications. The last water-based product included in this research, W6, is a 40 % active n-OTES. The corresponding solvent-based product S1 contains however 100 % n-OTES. The last organosilicon included in this research S2 is solvent-based and developed as an active component for formulating penetrating water

repellent treatments on mineral substrates. It is composed of both n-OTES and methyltrimethoxysilane (MTM) and is mostly applied at low concentrations by airless spraying, brushing or rolling onto the surface. It performs well at higher dilution rates and does not change the appearance of the substrate at low solids levels.

Table 1.1: Overview of all products used in this research, with their main components and active ingredient concentrations.

Product code	Main components	Concentration active ingredient (%)
Water-based organosilicons		
W1	DMS/n-OTES	50
W2	DMS/n-OTES	40
W3	PDMS	60
W4	PDMS/TES	100
W5	PDMS	60
W6	n-OTES	40
Solvent-based organosilicons		
S1	n-OTES	100
S2	MTM/ n-OTES	100
Biocides		
B1	IPBC	17
B2	Si-Quat	72
B3	IPBC/propiconazole	5/10

Depending on the test set-up these products were applied as delivered or diluted up to the desired concentration. Therefore demineralised water or the organic solvent isopropylalcohol was used for the water-based or solvent-based products, respectively.

Besides organosilicons also three biocides were included in the research. Main reason was to verify whether organosilicons are able to protect biocides from leaching and thereby guaranteeing a longer service life of the wood product (see further). The first fungicide is an emulsifiable formulation of 3-iodo-2-propynyl-butyl carbamate (IPBC, Troy Chemical Company, USA), while the second antimicrobial has the Si-Quaternary ammonium compound 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride (Si-Quat, Aegis Environments Inc, USA) as main component. Thirdly a biocide combining two

active ingredients was chosen, namely a 1:2 combination of IPBC and (±)-(cis+trans)-1-(2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl-methyl)-1H-1,2,4-triazole (propiconazole, Janssen Pharmaceutica, Belgium). It is a concentrate designed for use in formulating wood preservatives, wood stains, wood primers and blue stain agents. These biocides were all emulsifiable in water and isopropylalcohol.
The exact concentrations and combinations of products used throughout this research are explained each time under the Materials and Methods section of the appropriate chapter.

1.3.2 Application techniques

In this research different application strategies were applied, depending on the parameter which was to be examined. Basically the application techniques can be grouped into impregnating and superficial applications. The impregnations were performed on a laboratory or semi-industrial scale, merely depending on the sizes of the specimens to be treated. The superficial treatments were dipping or brushing of the specimens. Regardless the application technique, all specimens were always conditioned at 20 ± 2 °C and 65 ± 5 % relative humidity (RH) prior to treatment, unless otherwise mentioned.

For the impregnation at laboratory scale the procedure as recommended in EN 113 (1996) was chosen. First the specimens were put in a vessel under 0.8 bar vacuum for 20 minutes. Then the treating solution was allowed to flow into the vessel, until all specimens were completely submerged. After re-installing the vacuum for another 5 minutes, the vacuum was released and the specimens stayed submerged for 2 hours at atmospheric pressure. Upon removal of the specimens from the vessel they were weighed and dried first at ambient conditions for 48 hours and then at 60 °C until they reached constant mass. The specimens were not dried at 103 °C since there was some concern that the higher temperature could lead to loss of components and a poorer ability to compare results to large-scale treatments (Van Acker et al. 2003). The weight

percent gain (WPG) based on solution uptake was calculated based on the weight prior to and after treatment and on the concentration of active ingredient in the impregnating solution (ai_conc) (Eq. 1.1). The product retentions and retentions of active ingredients of both organosilicons and biocides were calculated using equations 1.2 and 1.3.

For the semi-industrial scale impregnations the specimens were submerged in the treating solution and a pressure of 4.5 to 5 bars was maintained for 45 minutes. Then the pressure was released while the specimens stayed submerged for another 15 minutes. Finally the specimens were removed from the pressure vessel and given 15 minutes to drain excess liquid. WPG and retention values were calculated in the same way as for the laboratory scale impregnated specimens.

$$WPG\ (\%) = \frac{m_{after\_impr}(g) - m_{before\_impr}(g)}{m_{before\_impr}\ (g)} \times ai\_conc(\%) \quad (1.1)$$

$$product_{ret}(kg/m^3) = \frac{m_{after\_impr}(g) - m_{before\_impr}(g)}{volume\ (cm^3)} \times \frac{ai\_conc(\%) \times 1.000}{conc\_active\_ingr(\%)} \quad (1.2)$$

$$active\_ingr_{ret}(kg/m^3) = \frac{m_{after\_impr}(g) - m_{before\_impr}(g)}{volume\ (cm^3)} \times ai\_conc(\%) \times 1.000 \quad (1.3)$$

Concerning the superficial application techniques dipping and brushing, they were very similar, as well as the calculation of their retention values. For the first technique the specimens were dipped for a few seconds in the treating solution, while for the latter procedure the specimens were brushed twice with the solution. Equations 1.4 and 1.5 give the way of calculating the product and active ingredient retentions of the organosilicons and/ or biocides.

$$product_{ret}(g/m^2) = \frac{m_{after\_application}(g) - m_{before\_appplication}(g)}{area\ (cm^2)} \times \frac{ai\_conc(\%) \times 10.000}{conc\_active\_ingr(\%)} \quad (1.4)$$

$$active\_ingr_{ret}(g/m^2) = \frac{m_{after\_application}(g) - m_{before\_appplication}(g)}{area\ (cm^2)} \times ai\_conc(\%) \times 10.000 \quad (1.5)$$

More precise parameters concerning the number of replicates, whether the specimens were (partly) sealed or not etc. are given under the appropriate heading of each chapter further in the work.

1.3.3 Economically feasible concentrations

As stipulated before, focus in this work was on treatments of wood which are economically feasible. Since organosilicon treated wood is not yet available on the market, it is difficult to say how much more a customer would want to pay for this kind of treated wood. In any case, a customer will always weigh the pros and cons against each other and be willing to pay more for a certain product as long as it generates sufficient benefits. This can be better performance, less maintenance, longer service life, a more attractive appearance, etc.

To determine this economically feasible concentration, there are several approaches possible. Firstly the same reasoning as for already commercially available improved wood can be applied. Generally it is accepted that this wood may cost 10 % more compared to its untreated counterpart. Usually less durable and widely available wood species like Scots pine are treated to make them more durable and fit for usage under higher risk exposure (use class 3). The low costs of these wood species put a constraint on the total cost of the treating solution, treatment process, energy costs, etc. Knowing that Scots pine costs about 250 €/m³ this would lead to an acceptable extra cost of 25 €/m³. Since the solvent-based products used in this research cost about 6 to 8 €/m³ this would correspond to circa 3.6 kg product per m³, ignoring even other costs. For the water-based emulsions, the prices vary more, namely between circa 5 and 20 €/m³, with an average of about 10 €/m³. This corresponds to a feasible retention of 2.5 kg product per m³.

The onset of this research was to find out whether organosilicon treated wood could be used outdoors, out of ground contact. In these use class 3 applications the treated wood should be able to meet the competition of wood species

having this natural durability by their own. This second approach assumes that the price of the organosilicon treated wood must be comparable to the price of wood species being moderately durable. Oregon pine, Douglas fir and oak are wood species having a natural durability of 3 and are easily available on the European market. Their prices are respectively circa 400 €/m³, 350 €/m³ and 750 €/m³. This means that on average the additional cost of the treatment may vary between 100 and 500 €/m³, being the higher cost price of the wood compared to Scots pine. More precisely at maximum 71 kg/m³ of solvent-based and 50 kg/m³ of water-based organosilicon could be added to Scots pine to remain economically feasible, again ignoring all other costs but the organosilicon itself. These product retentions correspond to circa 13 % WPG and 3.6 to 9 % WPG for the solvent-based and water-based organosilicons, respectively.

Further on in this dissertation it will be shown that for several wood evaluation parameters the wood preservatives approach is not the best one. The natural durability approach seems more suited. Therefore this last approach was used to determine the economically feasible concentration. Having these price levels in mind and allowing a deviation of about 10 % it was decided that only low concentrations of organosilicons would fulfil the economic requirements. That is why further on in this research in general the lowest concentration corresponding to 5 % active ingredient was used.

PART I

SILICON IN WOOD

Preface

Silicon, being the second most abundant constituent of the earth's crust (25.7 %), plays an important role in this world. It may account for up to 40 % of the soil mass, in contrast to levels in plant material which rarely exceeds 1 % and the tiny traces required by animals and humans. It is not considered essential for most higher plants but has a structural function in some lower groups. Silicic acid for example forms the basis of the protective shells of the microscopic diatoms.

The first men living on this planet soon found out that certain stones were easier to handle and more durable than others. They began to make tools and weapons out of them. The stone most used was flint, which is a form of silica or silicon dioxide (SiO_2). They used this material because it is very hard and tough. And this is also the reason why today we can still find artefacts made by people inhabiting this planet thousands of years ago. The latin name for flint is silex, silicis, and from this the name silicon for the chemical element Si and silica for its oxide SiO_2 is derived.

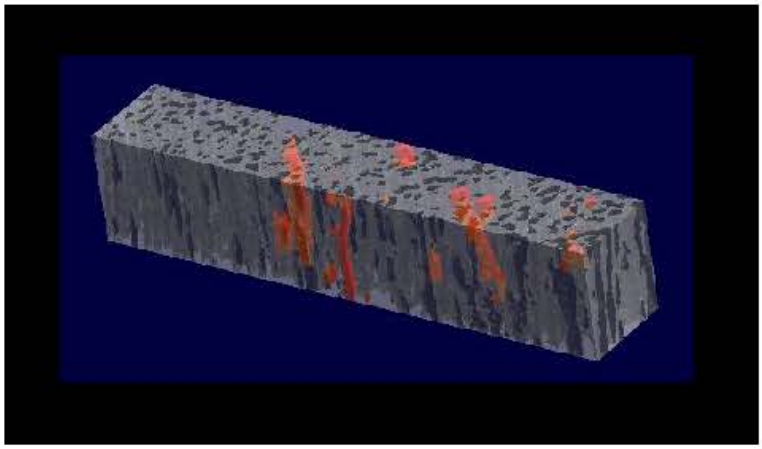
On the Table of Mendeljev silicon is situated somewhere in the middle, neither belonging to the metals, nor to the non-metals. It is a so-called metalloid, an element which looks like a metal, but does not act like one. Silicon has four electrons available for covalent bonding and has a very high affinity to oxygen with which it forms very strong chemical bonds. Unlike carbon it almost never forms double bonds. These and some other characteristics not mentioned here make this element unique, with properties suited for specific purposes. That is why it is wanted as a semiconductor and it forms useful glasses, cements and ceramics.

Silicon and its derivatives are being used in as many industrial and consumer applications as one can think of. Organosilicons for example have their usage as silicones in hair conditioners or are used in pre-treatment of textiles, making them soft to wear. They are being used to make mineral materials like concrete and mortars water repellent or as adhesion promoters between organic and inorganic materials. Organosilicons are also tipped as products having the potential to protect wood.

For treatment optimisation and tracing purposes after application or quality control it would therefore be interesting to know where the organosilicons can be found in the wood and at which concentrations. However, contrary to the wide range of applications, the ways of detecting organosilicons are limited. It was therefore the purpose in this first part of the work to find detection

techniques for the applied organosilicons. Firstly visualisation techniques using both destructive and non-destructive analyses were evaluated and combined with each other.

Secondary a quantitative method to determine the exact amount of Si present in the wood matrix was assessed. The main problem is that these organosilicons are insoluble. The goal is therefore to completely decompose the molecules and transform them into a soluble form, which can be detected more easily. Knowledge on penetration and concentration gradients of organosilicons in wood are important to enable further process optimisation, process quality control and fundamental understanding of the supposed interaction between wood and organosilicons.



2 DETECTION AND DISTRIBUTION ANALYSIS OF ORGANOSILICON COMPOUNDS IN WOOD BY MEANS OF SEM-EDX AND MICRO-CT[1]

Abstract

This research explores the potential of scanning electron microscopy with an energy dispersive X-ray spectrometer in combination with a new non-destructive 3D visualization technique, X-ray micro-computed tomography. In order to have a higher contrast, bromine functional silane was added to the mixture. Scots pine and beech samples were dipped or impregnated with an organosilicon and subsequently scanned. Both silicon and bromine were easily detectable with both techniques. Dipped organosilicons covered the cell walls partly in beech and the lumen partly or completely in Scots pine. Impregnated organosilicons in contrast could be found in the cell walls of both wood species. From the results, it can be concluded that, under the circumstances as described in this research, impregnation with an organosilicon is necessary to have cell wall penetration.

The combination of scanning electron microscopy, energy dispersive X-ray spectroscopy and micro-computed tomography can offer important information concerning the localization of certain products inside wood. While the last of these can monitor changes in 3D, the other two techniques can provide detailed 2D information. Both techniques are complementary and provide important extra information.

[1] Published as:
De Vetter, L., Cnudde, V., Masschaele, B., Jacobs, P.J.S. and Van Acker, J. 2006. Detection and distribution analysis of organosilicon compounds in wood by means of SEM-EDX and micro-CT. Materials Characterization 56: 39-48.

2.1 Introduction

Wood is since long an important building material. The wide variety in appearance, strength properties and the possibility of different dimensions are some of the reasons why wood is still very attractive for this purpose. Besides indoor use of wood, nowadays it is also frequently used as façade panelling or as garden furniture. These outdoor applications require, depending on the wood species, special wood protection. Older wood preservatives often use heavy metals such as copper, chromium and arsenic or are containing polyaromatic hydrocarbons like in creosotes (Kumar 1992; Buecker et al. 2003; Mai et al. 2003; Hill et al. 2004). Health care and environmental considerations make it no longer acceptable to use these preservatives which are based on broad spectrum biocides (Kumar 1992; Buecker et al. 2003; Mai et al. 2003; Hill et al. 2004). New wood preservatives face a lot of challenges: they should be easy applicable, guarantee a long lifetime to the wood and at the same time be easily broken down when released into nature.

Chemical wood modification is a compromising approach, not just to enhance the durability against fungi and insects, but also to improve further material properties such as dimensional stability, strength, moisture sorption, flammability, UV-stability and weathering performance (Kumar 1992; Militz et al. 1997; Suttie et al. 1998; Mai et al. 2003; Van Acker 2003; Donath et al. 2004). A group of chemicals which are also suitable for this are the polymers. The idea is that they penetrate the cell wall as monomers and polymerise in situ. Since the cell wall is swollen with polymers, the dimensional stability is enhanced. When on top of that the polymer is not hydrophilic, the rate and ultimate uptake of moisture are both reduced. Finally the ingress of fungal metabolites capable of degrading the wood cell wall polymeric components is reduced or prevented, since the impregnated polymer is able to block the cell wall micro-porous network through which these agents diffuse (Eaton and Hale 1993).

Silicone compounds and more specific silanes and/or siloxanes are already used in many researches as a possible group of suited chemicals (Schneider

and Brebner 1985; Mai et al. 2003; Ritschkoff et al. 2003; Donath et al. 2004; Hill et al. 2004). They are frequently used as a water repellent product for natural building stones (Cnudde et al. 2009). Since the localization of these products inside wood is essential in the research of wood protection a first step in the evaluation of these products is to try to localize the silanes and/or siloxanes in treated wood. The object of this study is to evaluate the potential of scanning electron microscopy with an energy dispersive X-ray spectrometer (SEM-EDX) in combination with a new non-destructive 3D visualization technique, X-ray micro-computed tomography (micro-CT), as detection methods for silanes/siloxanes mixtures applied in different types of wood.

X-ray micro-CT, a powerful tool in material research, was already successfully applied within the scope of wood anatomical research by Steppe et al. (2004). Cnudde et al. (2004) illustrated the possibility of the visualization of silane-based products inside stone material by means of micro-CT. Since the visualization of the products inside wood is based on the same principle as for the visualization of products inside stone material, the micro-CT technique was selected for this research. The big advantage of this non-destructive technique, which visualizes the internal microstructure of the scanned samples in 3D, is the fact that it provides the possibility to scan the samples before and after treatment with silanes/siloxanes mixtures. After scanning with micro-CT, the same specimen can be analysed by SEM-EDX to obtain a complete distribution mapping of silicone compounds in wood and to make a firm link between both methods.

2.2 Materials and methods

2.2.1 Materials

Because of the important differences in anatomical structure between softwood and hardwood species, one species of both groups was chosen. Scots pine

sapwood (*Pinus sylvestris* L.) and beech (*Fagus sylvatica* L.), both reference wood species in many European Standards dealing with wood preservation, were used. For every treatment technique one specimen was evaluated.

The siloxane used is a hydroxyterminated polydimethylsiloxane from the company Dow Corning. It is a water dilutable emulsion with an organosilicon content of 60 %. This commercial product is also used as a mould release agent and applied in low concentrations by spraying or dipping. In this research it was applied both by dipping and impregnating at a concentration as low as 5 % silicone content.

To obtain a high contrast with micro-CT between wood and siloxane, mixing the siloxane was chosen as a possibility to increase this contrast. Based on the previous study of Cnudde et al. (2009) on the doping of siloxane mixtures, 3-bromopropyltrimethoxysilane (Figure 2.1) was selected as possible mixing component for the visualization of the silanes inside the wood material. The presence of the bromine atom on the 3-bromopropyltrimethoxysilane causes a higher attenuation of X-rays and the wood, resulting in a better contrast on the micro-CT images.

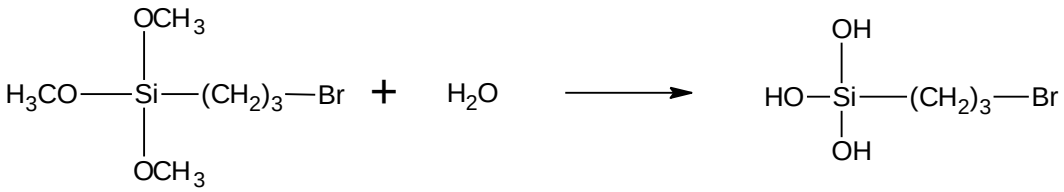


Figure 2.1: Chemical structure of 3-bromopropyltrimethoxysilane

2.2.2 Treatments

In a first attempt to localise silica with SEM-EDX a beech and Scots pine sapwood sample with dimensions 40 × 40 × 5 mm (T × R × L) were impregnated with a 5 % concentration of the hydroxyterminated

polydimethylsiloxane. Afterwards the sample was divided into 40 small cubes measuring 5 × 5.6 × 5 mm (T × R × L).

In order to have a clear contrast between wood and siloxane, samples were treated with an aqueous mixture of 5 % siloxane and 20 % 3-bromopropyltrimethoxysilane. Firstly part of a beech and Scots pine sample with dimensions 30 × 5 × 5 mm (T × R × L) and an orientation of the growth rings of approximately 45°, were immersed in the solution The lowest 10 mm of the samples were dipped for 1 minute in the aqueous treating solution. Afterwards they were dried upright under atmospheric conditions. The second treatment was a vacuum impregnation in the aqueous treating solution. Specimens' sizes were 6 × 6 × 13 mm (T × R × L) and the growth rings had an orientation of approximately 45°.

2.2.3 Scanning electron microscopy

A scanning electron microscope (FEI Company Quanta 200F) was used to examine surface details of the scanned wood. By means of an energy dispersive spectrometer (EDX), qualitative and quantitative compositional analysis could be obtained and precise elemental composition of materials with high spatial resolution was accomplished. Secondary electron imaging was used to analyse the morphology and the surface topography of the samples, while backscattered electron imaging visualized compositional contrast in detail. SEM was already previously used to scan silica in rattan species (Abasolo et al. 2001) and solid wood (Zollfrank and Wegener 2002).

To avoid electron loading of the samples, the surface was sputtered with a gold layer. All images were made under high vacuum at a voltage of 20.0 kV with a spot size of 4 to 6 nm, a dwell of 3000 µs and a working distance of 10 mm. The EDX detector has an elevation angle of 35°. In order to obtain a surface as smooth as possible, the samples were first scanned with the micro-CT to be

sure the borders were included. They were then surface cut with a microtome and subsequently scanned with the SEM-EDX.

2.2.4 Micro-CT

An X-ray desktop micro-tomograph Skyscan 1072 was used to scan the small wood cubes of 30 × 5 × 5 mm (T × R × L). The X-ray source, a Hamamatsu micro-focus tube, has a focal spot size of 10 µm, which limits the spatial resolution of the reconstructed slices to 10 µm in the X, Y and Z directions. The samples were scanned at a voltage of 130 kV, a current at 76 µA and an exposure time of 2.3 ms. A rotation step size of 0.45°, in combination of random movement and multiple-frame averaging was used to minimise the Poisson noise in the images. The magnification was chosen in such a way that the pixel size reached 10.10 µm. Since this magnification allows visualisation of volumes up to 12 mm long, the dipped samples were divided into three parts: a lower part which was completely dipped in the solution (0-9 mm), a middle part where the bottom was dipped and the top was not (9-18 mm) and an upper part of untreated wood (18-30 mm). The impregnated samples were small enough to be scanned as a whole.

The images were reconstructed with Octopus, which is a server/client tomography reconstruction package for parallel and cone beam geometry (Dierick et al. 2004).

2.3 Results and discussion

2.3.1 Impregnation with siloxane

In order to have an idea of the penetration depth of the siloxane into the wood, a corner and central block were scanned with SEM-EDX at all sides. The SEM images give a clear view of the anatomical characteristics of both beech and Scots pine. Tissue types like earlywood, latewood and the characteristic large

wood rays of beech can easily be distinguished on the transverse image. Since Scots pine does not have such large wood rays as beech, they cannot be spotted, but resin canals on the other hand, can clearly be seen. Even individual cells and bordered pits can be distinguished.

A first glance on the resulting EDX images indicates the silicone can be found on all sides of the wood cubes over the entire surfaces. For the corner block this seems self-evident. The fact that the same observation is true for the central block indicates the silicone has penetrated even into the heart of the wood block. Moreover, the anatomical structure of the wood is apparent on the EDX images. The explanation for this can be found at larger magnification. At cell level no silicone is detected in cavities, such as the cell lumens, and so they are left dark, whereas cell walls do light up indicating they contain silicone. Beech has larger lumens which are easily detected whereas the lumens of Scots pine tracheids are smaller and a lot of small, darker spots on the EDX images can be seen.

2.3.2 Detection

The main goal of this research is to try to detect siloxanes in siloxane-treated wood. Wood always contains a small amount of silica (Istas and Raekelboom 1952; Grimshaw et al. 1974). A comparison of images of treated and non-treated wood showed this natural amount of silica is too low to detect. Depending on the abundance and form of the siloxanes they can be seen already at magnification 220. Zooming in on the siloxanes reveals the structure consists of a microporous network, this means a 3D structure with pores of varying sizes (Figure 2.2). The siloxanes are found in different forms and dimensions: ranging from a thin layer on the cell walls to big props filling the lumens. Because of this network EDX-mapping isn't always necessary to detect the siloxane; the network contrasts very well with the normal wood structure. EDX-mapping showed the network consists of the elements Si (siloxane) and Br (mixing agent).

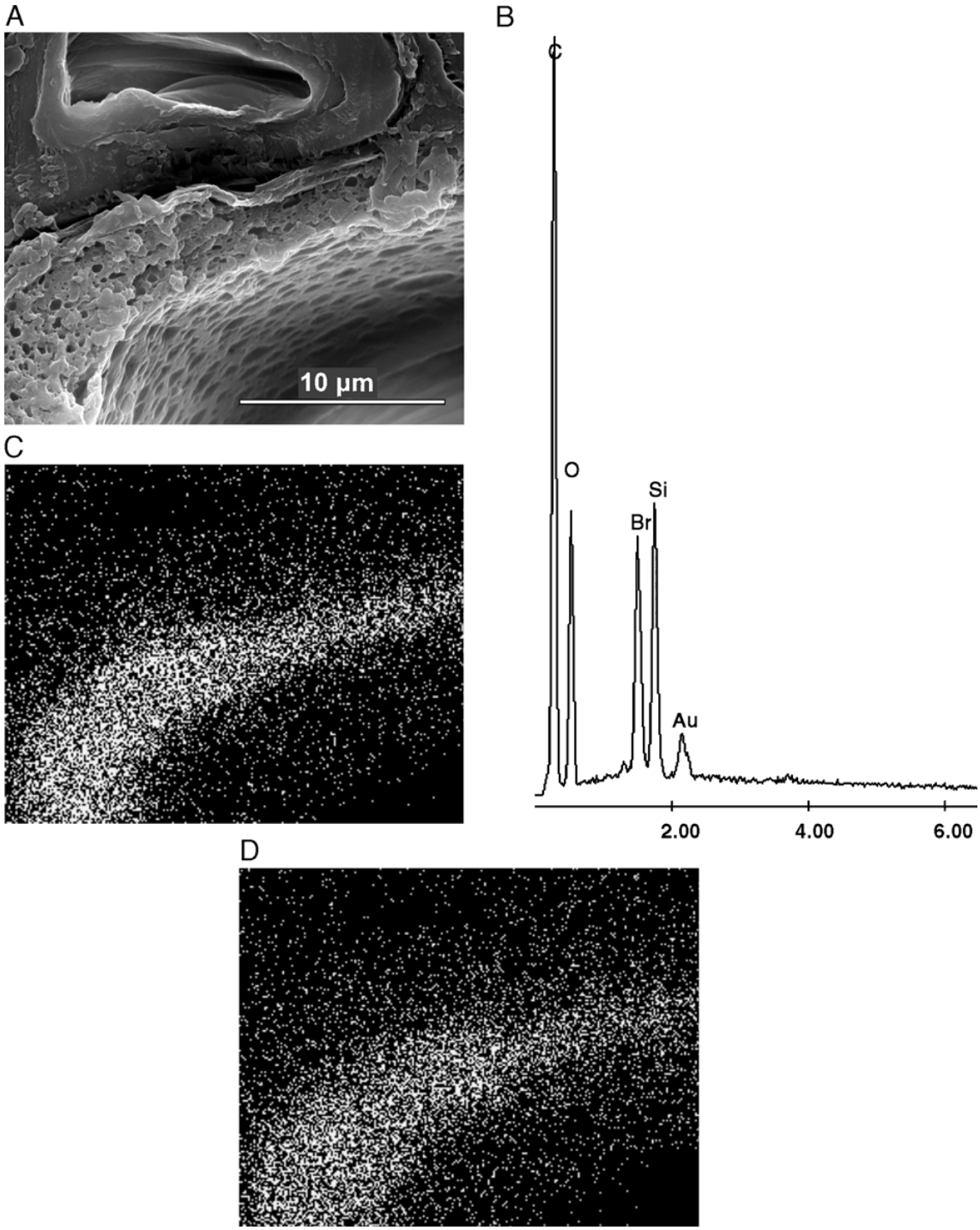


Figure 2.2: SEM image (A) and corresponding spectrum (B), and the Si-K (C) and Br-L (D) X-ray maps taken in the same areas on transverse sections of beech dipped in a siloxane/silane mixture

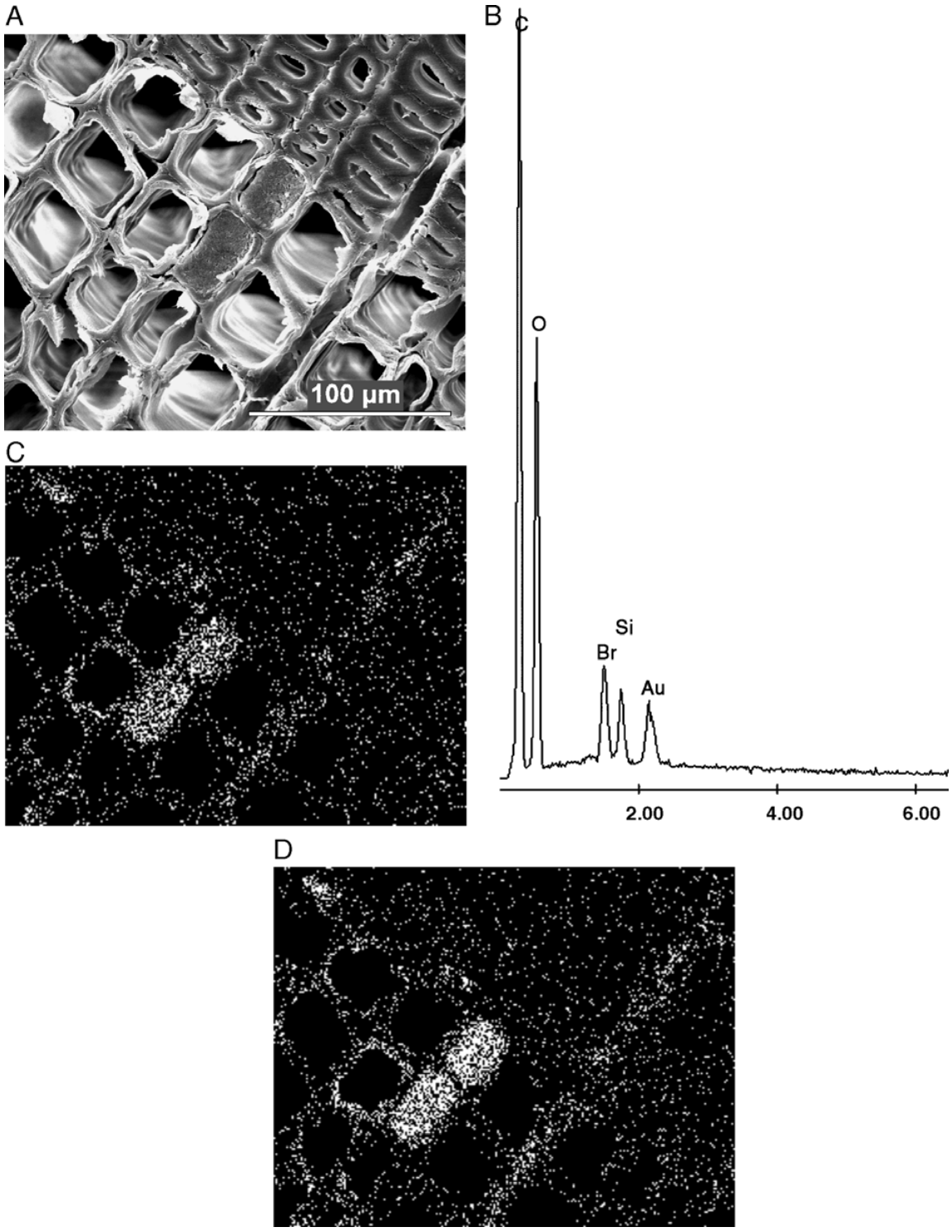


Figure 2.3: SEM image (A) and corresponding spectrum (B), and the Si-K (C) and Br-L (D) X-ray maps taken in the same areas on transverse sections of Scots pine dipped in a siloxane/silane mixture

2.3.3 Siloxane/silane mixture dipped specimens

Transverse scanning of beech reveals a micro-porous network at the inside of some vessels. This network follows the longitudinal direction and can vary in thickness from less than 1 µm to more than 3 µm. It does not cover the entire area of the cell walls of the vessels, but leaves some parts and bordered pits uncovered (Figure 2.2).

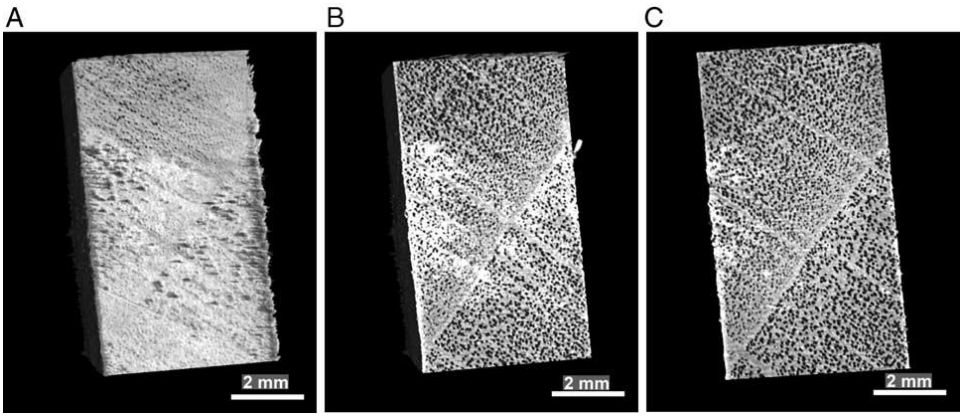


Figure 2.4: Transverse image of beech dipped in a siloxane/silane mixture at three different positions: (A) border, (B) crosscut close to the border and (C) crosscut in the middle of the sample

A transverse image of Scots pine (Figure 2.3) seems somehow different from that of beech (Figure 2.2). Silicon is not evenly distributed over the entire area. Most signals are found in the larger structures: the tracheids of the earlywood and the wood rays. In some tracheids no signal of silicon or bromine could be detected. In others a thin film of the micro-porous network covers the cell wall, and in again some others the micro-porous network fills the lumen partly or even completely. The walls of most wood rays are covered by the network. The props formed by siloxanes in the lumen of tracheids are not indissoluble connected to the cell walls. Moreover, some props loosened (maybe due to microtoming) and formed new cavities. The cell walls themselves only seem to have taken up the bromine and silicon in small contents. At higher magnification no silicon can be found in the middle lamella.

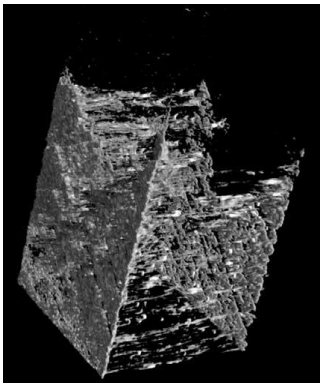


Figure 2.5: 3D reconstruction of a siloxane/silane mixture (visualized) in penetrating dipped beech (not visualized)

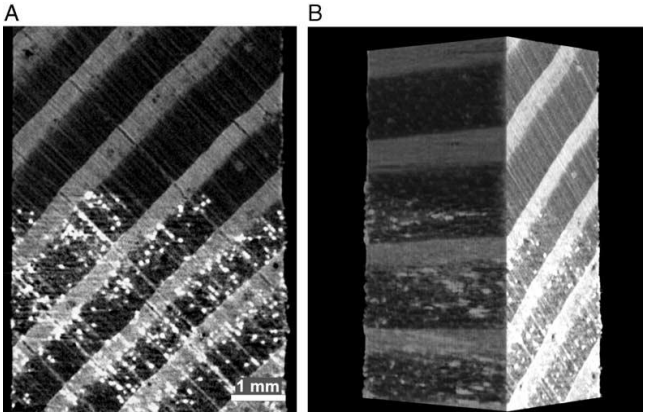


Figure 2.6: Dipped Scots pine: (A) crosscut in the middle and (B) 3D reconstruction

The resolution of the micro-CT is not high enough to distinguish the siloxane/silane mixture inside the wood in the same detail as SEM-EDX (Figures 2.4, 2.5 and 2.6). On the other hand, the images derived from the micro-CT indicate a global overview of the sample in 3D with the distribution of the mixed product. More than 1000 cross-sections with an in between distance of 10.10 µm are obtained from each scanned wood sample, offering the possibility to look inside the wood in a non-destructive way. Additionally, since the sample sides need to be cut with a microtome before scanning with the SEM, information of siloxanes at the sides can only be derived from the micro-CT images.

Looking at the 3D reconstructions after micro-CT, the transitional part of the sample (where the bottom was dipped and the top was not) offers some very interesting information. Figures 2.4 and 2.5 show a part of this transition zone for beech. Migrating from the exterior to the interior a decrease in siloxane is observed. As Figure 2.5 illustrates, most siloxane/silane can be found at the borders and the penetration of the mixture took mainly place in the longitudinal direction. These images are thus a confirmation of the SEM-images.

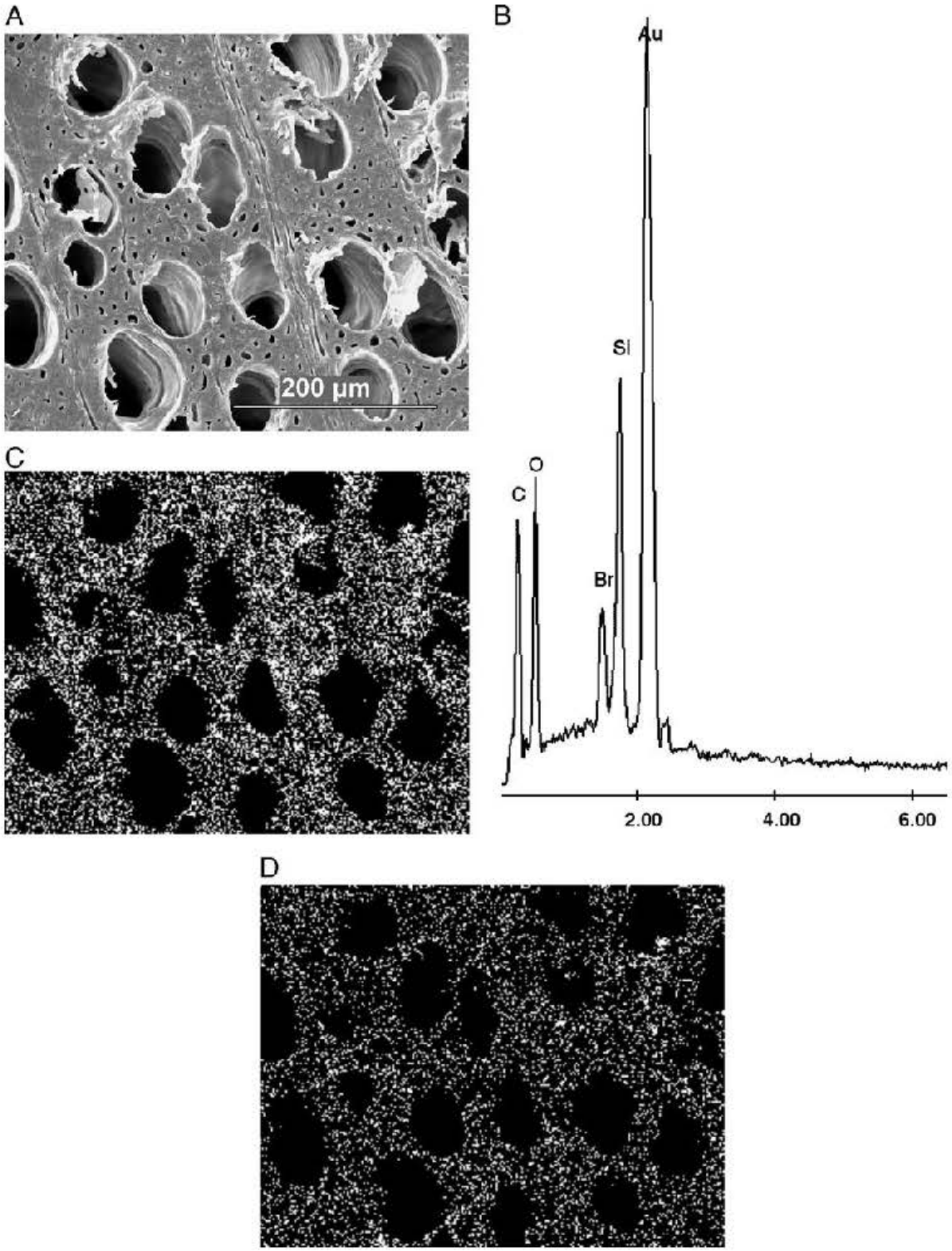


Figure 2.7: SEM image (A) and corresponding spectrum (B), and the Si-K (C) and Br-L (D) X-ray maps taken in the same areas on transverse sections of beech impregnated with a siloxane/silane mixture

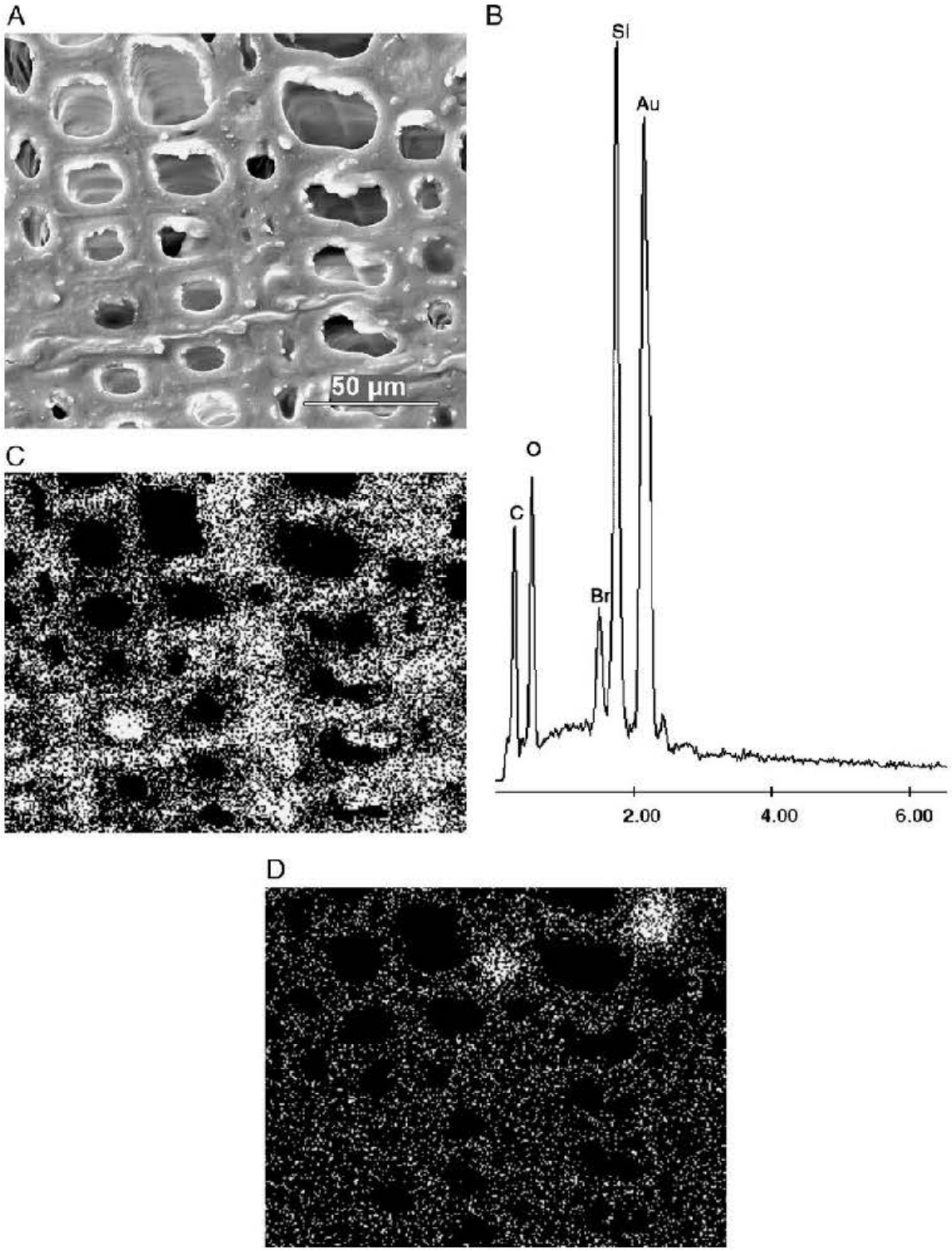


Figure 2.8: SEM image (A) and corresponding spectrum (B), and the Si-K (C) and Br-L (D) X-ray maps taken in the same areas on transverse sections of Scots pine impregnated with a siloxane/silane mixture

The penetration front of the siloxane/silane mixture in Scots pine is distinct on Figure 2.6. The figure clearly shows some tracheid lumens are filled with the mixture, whereas others are not. As in beech micro-CT seems a complementary technique in evaluating penetration depth and patterns in treated wood.

2.3.4 Siloxane/silane mixture impregnated specimens

As in the dipped samples silicon and bromine are easily detectable with SEM-EDX. In contrast although, the elements are not found as a thin layer on the cell walls or in the lumens, but inside the cell walls themselves (Figure 2.7 and Figure 2.8). Remarkable is the fact that silicone and bromine do not always appear to be on the same spots. So it must be concluded there was no homogenous mixture of the hydroxyterminated polydimethylsiloxane and the 3-bromopropyltrimethoxysilane. Better formulations could be evaluated to resolve this problem.

One vessel of beech shows an interesting detail (Figure 2.9). Zooming in at magnification 4000 reveals a bubbled layer on the inner surface. A possible explanation of this peculiar phenomenon is that the layer itself is a siloxane (proved by SEM-EDX) formed due to the impregnation. However volatile compounds included in the cell wall, like water vapour, came out of the cell wall afterwards and formed bubbles under the siloxane layer.

The 3D reconstructions after micro-CT scanning show the siloxane/silane mixture can be found all through the samples of beech and Scots pine (Figures 2.10 and 2.11). Just like in dipped beech, Figures 2.10 a and b indicate most siloxane/silane in impregnated samples is to be found at the borders of the sample. The vessels stay open, but the cell walls contain the mixture. The wood rays of Scots pine seem to contain more siloxane/silane than the surrounding tissues (Figures 2.11 a and b). This is a confirmation of the SEM-EDX results.

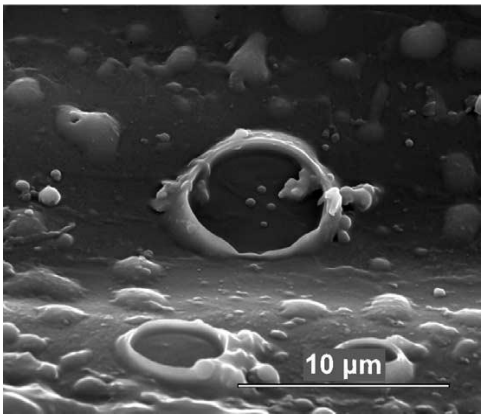


Figure 2.9: SEM image of the inside of a vessel of siloxane-bromine mixture impregnated beech

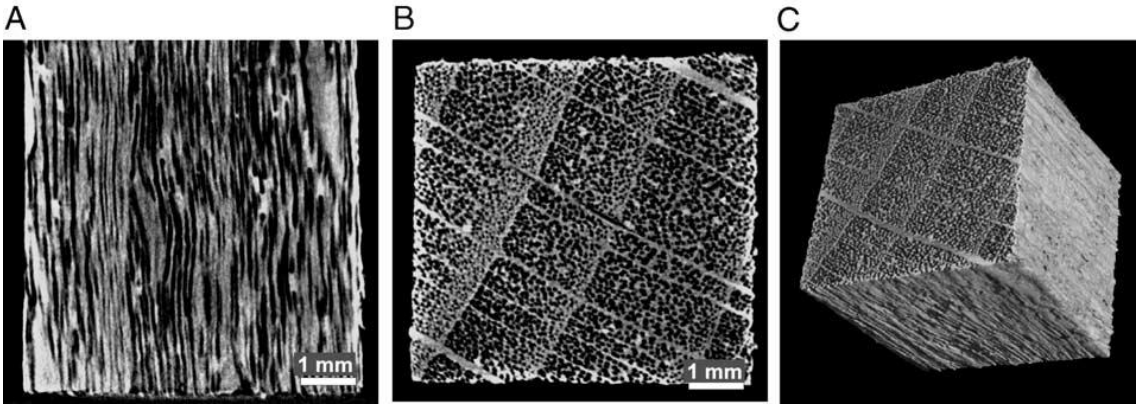


Figure 2.10: Reconstruction of siloxane/silane impregnated beech: (A) longitudinal image, (B) transverse view and (C) 3D view

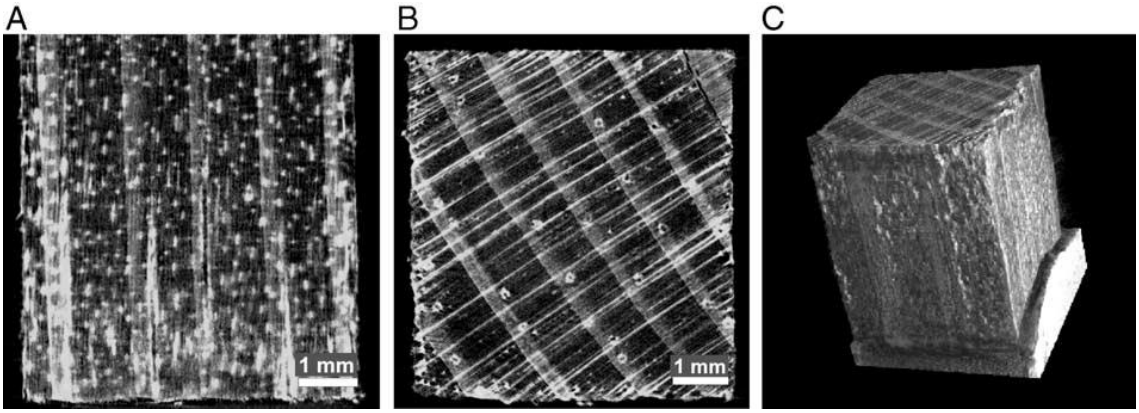


Figure 2.11: Reconstruction of siloxane/silane impregnated Scots pine: (A) longitudinal image, (B) transverse view and (C) 3D view

2.4 Conclusion

SEM is able to give a clear view of the anatomical structure of wood. Mapping with EDX makes it possible to see with very good detail where silicon, originating from siloxanes, can be found. This is mainly in the lumen for dipped wood and in the cell wall for wood impregnated with the hydroxyterminated polydimethylsiloxane.

X-ray micro-computed tomography is indeed a powerful tool in getting a 3D image of the structure of (non-)treated wood. The border between treated and non-treated wood is very clear and an idea about the concentration can be derived based on the intensity of the gray values. The combination of SEM-EDX and micro-CT can offer important information concerning the localization of certain products inside wood. While micro-CT can monitor changes in 3D, SEM-EDX will give detailed 2D information. Both techniques are complementary and using both techniques provides important extra information. Since technology is improving fast, micro-CT which is still limited by its resolution, will be enhanced by the development of nano-CT, with a resolution up to 400 nm. This technique is still in its early development, but will turn out to be very useful for more detailed 3D research.

From the experiment results it can be concluded that, under the circumstances as described in the article, impregnation with a siloxane is necessary to have cell wall penetration. This is an important factor to keep in mind when trying to achieve wood protection with siloxanes.

Acknowledgments

The authors wish to express their gratitude to Dr. Andreas Stammer (Dow Corning Company) for supplying the hydroxyterminated polydimethylsiloxane. They also wish to thank Olivier Janssens for the technical support (Ghent University, Department of Solid State Sciences). This research was carried out to support the European Project Improvement of wood product properties by increased hydrophobicity obtained by the use of silicon compounds, with acronym HYDROPHOB (QLK5-CT-2002-04139).

3 QUANTITATIVE DETERMINATION OF SI IN ORGANOSILICON TREATED WOOD

3.1 Introduction

When wood is being treated with a certain product it is interesting to trace the product inside the wood. The knowledge on where how much product can be found is important for process optimisation as well as quality control. Since the use of organosilicons in the wood area is new, no specific methods for this purpose exist yet and methods from other research areas should be adopted.

Silicon is naturally present in most plants and certain wood species under the form of silica, silicates or silica grains (Hawley and Wise 1954; de Silva and hillis 1980; Patel 1986; Abasolo et al. 2001; Motomura et al. 2002). The amounts of these inorganic substances can be detected in several ways (Abasolo et al. 2001). But with organic silicon extra concern is needed. First of all they are often highly volatile and secondly they have the tendency to form some silicon carbide instead of silicon dioxide on combustion (McHard et al. 1948). Already in the early years of commercial production of organopolysiloxanes these problems were recognised and research was started to find a proper method for tracing the Si back. The first step in any determination is decomposing the material so as to destroy the organic matter and release silicon (Grimshaw 1974).

The approaches used can be generally classed in three groups: wet oxidation, dry combustion, and fusion (McHard et al. 1948). This last technique seemed promising and both acid and alkali fusions were tried out (McHard et al. 1948; Wetters and Smith 1969; Haken 1993). Direct alkali fusions were performed with sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) as well as potassium hydroxide (KOH) (Mori 2003). This way the alkyl or aryl groups from silicon are removed and silicates are produced (Wetters and Smith 1969). Upon addition of hydrochloric acid (HCl) the silicates are transformed to silicic acids (Grimshaw et al. 1974). These can subsequently be evaluated using gravimetric or spectrophotometric analyses (Wetters and Smith 1969; Grimshaw 1974), as is often used for the determination of reactive silica in water (Morrison and

Wilson 1963; Greenberg et al. 1992; Giacomelli et al. 1999). This last technique is more sensitive and therefore preferred (Grimshaw 1974).

Generally the silicates react with ammoniummolybdate in an acidic environment and form a yellow silicomolybdic complex. This complex has two isomers depending on pH but both have only low intensity colours. That is why several methods have been developed in which the complexes are reduced to intensely coloured blue complexes, being more sensitive than the yellow method (DeEds and Eddy 1936; Korenaga and Sun 1996). Several inorganic and organic reducing agents have been used, but an acid mixture of methol (p-methylaminophenol sulphate) and sulphite (Na_2SO_3) is the most common one (Koroleff 1976). Phosphorus may interfere and form molybdophosphoric acid (Morrison and Wilson 1963), but this interference is prevented by pH control and the presence of oxalic or tartaric acid (Grimshaw et al. 1974; Furlani and Gallo 1978). This so-called heteropoly blue method was found suitable to determine Si in sea water (Koroleff 1976; Greenberg et al. 1992), soils (Morrison and Wilson 1963), food (Dejneka and Łukasiak 2003), rocks (Rao et al. 1992), plant material (Woolley and Johnson 1957; Boltz and Howell 1978; Furlani and Gallo 1978), bamboo (Sulthoni 1989; Leroy 1998) and bamboo leaves (Motomura et al. 2002).

3.2 Materials and methods

For the quantitative determination of Si in wood resulting from organosilicon treatment, Scots pine sapwood (*Pinus sylvestris* L.) and beech (*Fagus sylvatica* L.) specimens measuring 30 × 30 × 5 mm (R × T × L) were vacuum impregnated with 5 % or 10 % concentration of an organosilicon ($conc_{organosilicon}$). Therefore the water-based products W1, W2 and W5 were chosen. Detailed information about the products and the application procedure can be found under the heading 1.3. The Si-contents of W1, W2 and W5 are, according to producers' information, respectively < 5 %, 11.2 % and 22.7 %

($conc_{Si\_in\_organosilicon}$). Considering the mass prior to and after impregnation allows calculating the theoretical Si-content of each wood block (Eq. 3.1).

$$m\%\ Si = \frac{(m_{treated} - m_{untreated}) \times conc_{Si\_in\_organosilicon}}{m_{untreated} \times 10.000} \quad (3.1)$$

In this research the spectrophotometric determination of Si with the molybdenum blue method as described by Leroy (1998) was chosen since it was the most recent method for detection of Si in bamboo, being the material closest to wood. The treated wood blocks were per treatment grinded to wood powder through a sieve of grid 1 mm, and mixed thoroughly afterwards. A sample of 0.5 g of each powder was alkali fused in a nickel crucible with 5 ml 10 % NaOH and pyrolysed at 700 °C for 4 hours. After cooling down the residue was solved in distilled water and transferred to a volumetric flask. Subsequently 5 ml HCl 12 N was added and the solution was further diluted with H_2O till 250 ml. Then 20 ml of this powder solution was transferred to a volumetric flask of 50 ml and 2 ml ammoniummolybdate reagent (5 g $(NH_4)_6Mo_7O_{24}.4H_2O$ (ammoniumheptamolybdate-tetrahydrate) solved in 50 ml H_2O with 5 ml H_2SO_4 95-97 % and diluted till 100 ml with H_2O) was added. After shaking the solution was given 10 min to rest. Afterwards 2 ml tartaric acid (5 g $C_4H_6O_6$ in 50 ml H_2O) was added and the flask was shaken again. Consequently 2.5 ml H_2SO_4 10 N and 2 ml reducing agent (30 g $Na_2S_2O_5$ and 3 g Na_2SO_3 in 200 ml H_2O; 0.5 g methol (p-methylaminophenol sulphate) in 25 ml H_2O; fuse both solutions and dilute till 250 ml with H_2O) were added, the solution was shaken and further diluted till 50 ml with H_2O. After 30 min the absorbance was measured at 828 nm. A silicon standard solution of SiO_2 in NaOH (0.5 mol/l 1000 mg/l Si) was used to make a concentration series. The same procedure except for pyrolysation, dissolution and acidification was carried out on the concentration series. The absorbance values were used to recalculate the amount of Si present in each sample.

3.3 Results and discussion

Figures 3.1 and 3.2 show the Si-concentrations in function of the measured absorption found in 0.5 g of treated Scots pine sapwood and beech, respectively. Both figures show a big spread on the values both for treated as well as untreated wood. For Scots pine sapwood values between 0.006 and 0.184 Wt % SiO_2 are recorded, while the range for beech is between 0.086 and 0.513 Wt % SiO_2. Besson (1946) found 0.0043 Wt % SiO_2 in beech and Istas and Raekelboom (1967) reported SiO_2 contents of 0.07 Wt % for pine from Belgium and values ranging from 0.01 to 0.04 Wt % SiO_2 for pine from Poland and Finland. Generally speaking the order of magnitude of SiO_2 concentrations of beech and Scots pine are similar for the data presented here and the corresponding ones from literature. However, high variability in the Si-values and the overlap between the values for untreated and treated wood can be seen on both figures. Especially for beech overlap exists between untreated wood and wood treated with 5 % and 10 % concentrations of organosilicons.

It is therefore assumed that the background concentration of Si present in untreated wood is detected, but that most of the organosilicon added is not properly transformed and detected by the performed method. Figures 3.1 and 3.2 show that the highest amounts of Si are found for wood treated with W5, followed by wood impregnated with W2 and finally by wood treated with W1. These last give Si concentrations comparable to those found in untreated wood. This order in organosilicons was expected, since it is the same as the order of Si-content of the organosilicons. The figures further indicate that for a certain organosilicon no clear distinction between the 5 % and 10 % concentrations can be seen.

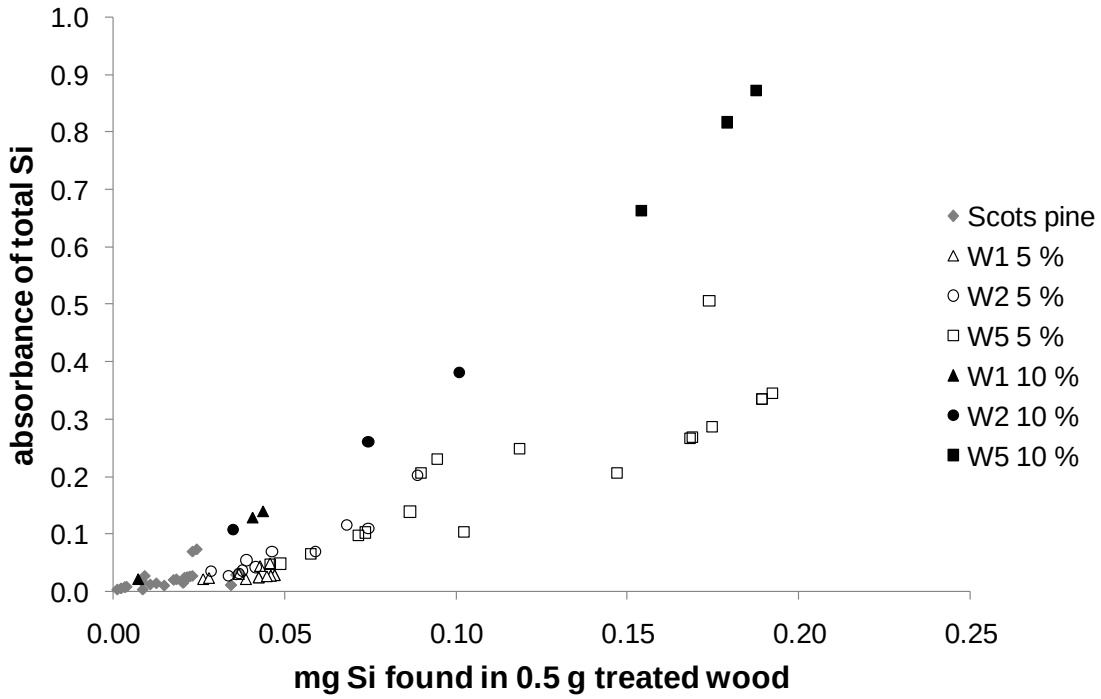


Figure 3.1: Absorbance of total Si found in milled untreated Scots pine sapwood and Scots pine sapwood impregnated with 5 % or 10 % of an organosilicon (W)

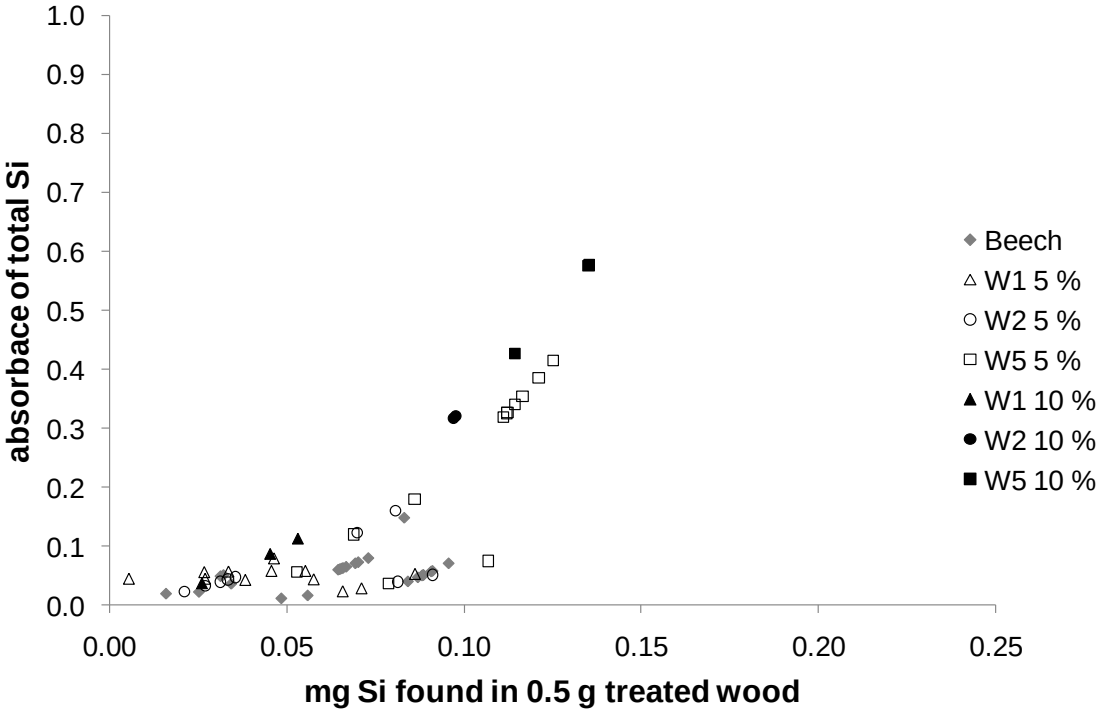


Figure 3.2: Absorbance of total Si found in milled untreated beech and beech impregnated with 5 % or 10 % of an organosilicon (W)

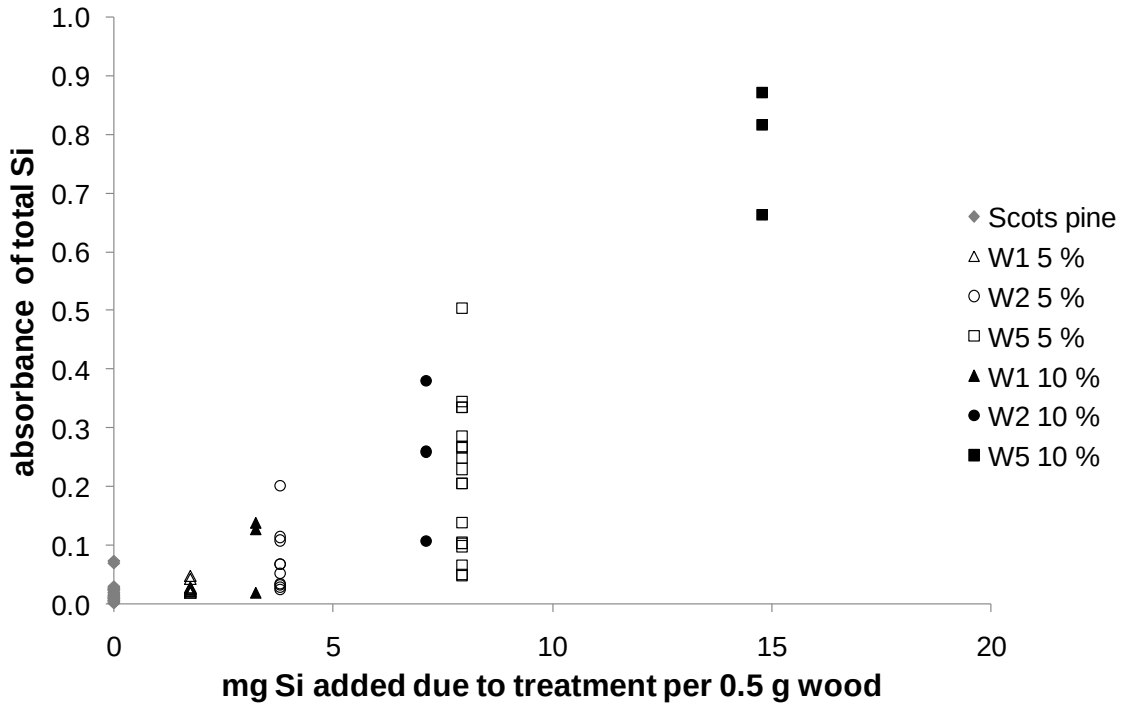


Figure 3.3: Absorbance of total Si present in milled Scots pine sapwood in function of the theoretical amount of Si added due to organosilicon-impregnation (W) of the wood

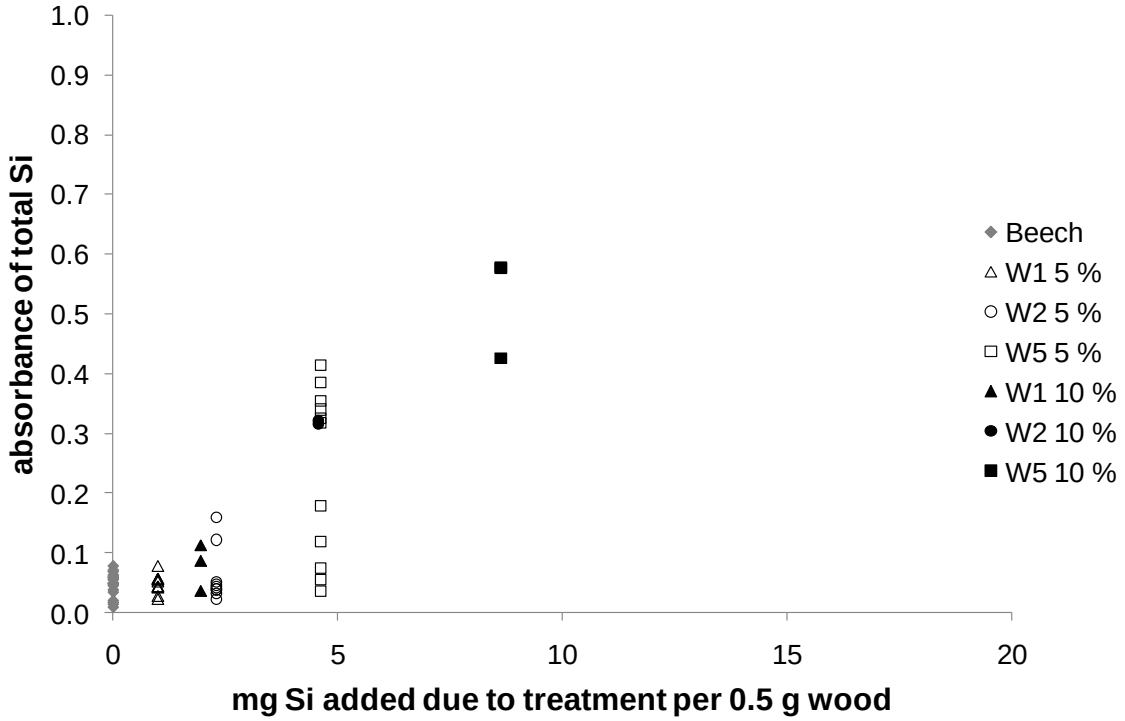


Figure 3.4: Absorbance of total Si present in milled Scots pine sapwood in function of the theoretical amount of Si added due to organosilicon-impregnation (W) of the wood

It was found valuable to calculate the theoretical amount of Si added due to treatment. They were also put in function of the absorbance measured. Figures 3.3 and 3.4 show that for each theoretical Si-concentration added to the wood, a broad range of corresponding absorbance values was found. Although the sampled material was each time the same, the analysis was performed over several days for practical reasons. It can therefore be assumed that not all Si was properly transformed and made detectable by the method each time. The minimum and maximum recovery rates were calculated per treatment and are given in Table 3.1.

Table 3.1: Minimum and maximum recovery rates (%) of Si added due to impregnation of Scots pine sapwood and beech with 5 % and 10 % concentrations of three organosilicons (W) and traced back with the molybdenum blue method

	Scots pine sapwood				Beech			
Concentration	5 %		10 %		5 %		10 %	
Treatment	min	max	min	max	min	max	min	max
W1	1.50	2.69	0.22	1.35	0.55	8.62	1.33	2.72
W2	0.75	2.34	0.49	1.42	0.93	3.97	2.14	2.13
W5	0.58	2.38	1.04	1.27	1.15	2.71	1.33	1.57

To check whether the low recovery rates are due to an improper transformation of organic Si into silicates, a pure organic and a pure inorganic Si-containing solution were purchased and analysed twice in the same way. Afterwards slight changes to the method were introduced (1) the warming up phase of the muffle furnace was normally 1 hour, but was once spread over 4 hours; (2) the products were analysed without being pyrolysed, acidified and dissoluted. Table 3.2 shows the obtained recovery rates for the different methods and solutions. The table shows that the recovery rates diminish with increasing Si-content, and this regardless the kind of Si present in the solution. Furthermore extremely high recovery rates are found when low concentrations of organic Si are analysed. The importance of the pyrolysation phase and the circumstances at which this is performed is shown by the last two methods. Heating in the muffle furnace 4 hours instead of 1 hour at 700 °C, reduces the recovery rate considerably, both for organic as well as for inorganic Si. When no pyrolysation

at all is done, the recovery rates further diminish, although it must be said higher concentrations were tested under these circumstances.

Table 3.2: Recovery rates for the detection of Si from both inorganic and organic Si-containing solutions performed with the molybdenum blue method as described by Leroy (1998) and two variations on the procedure

Deviation from method of Leroy (1998)	None – Trial 1	None – Trial 2	Heating 4 hours	No pyrolysation or acidification
Inorganic Si (SiO_2)				
Range of Si (mg)	0.04 - 0.32	0.04 - 0.32	0.04 - 1.3	0.50 - 4.00
Recovery (%)	77.75 - 39.88	104.75 - 30.59	9.96 - 7.63	1.63 - 2.61
Organic Si (PDMS fluid)				
Range of Si (mg)	0.04 - 0.32	0.04 - 0.33	0.05 - 2.67	0.50 - 4.01
Recovery (%)	147.38 - 41.93	150.22 - 20.53	28.01 - 1.31	0.74 - 0.37

The twenty three standard curves used to recalculate the amounts of Si present in each sample are represented in Figure 3.5. The figure gives the amounts of Si present in the standard solutions and the corresponding absorbances measured. The figure indicates that the range was broad enough to cover all Si-contents found in the samples, but that the standard curves were not linear (R^2 values between 66.69 and 98.06). Therefore a regression line of second order was used to recalculate the Si-contents measured (R^2 between 92.29 and 99.89).

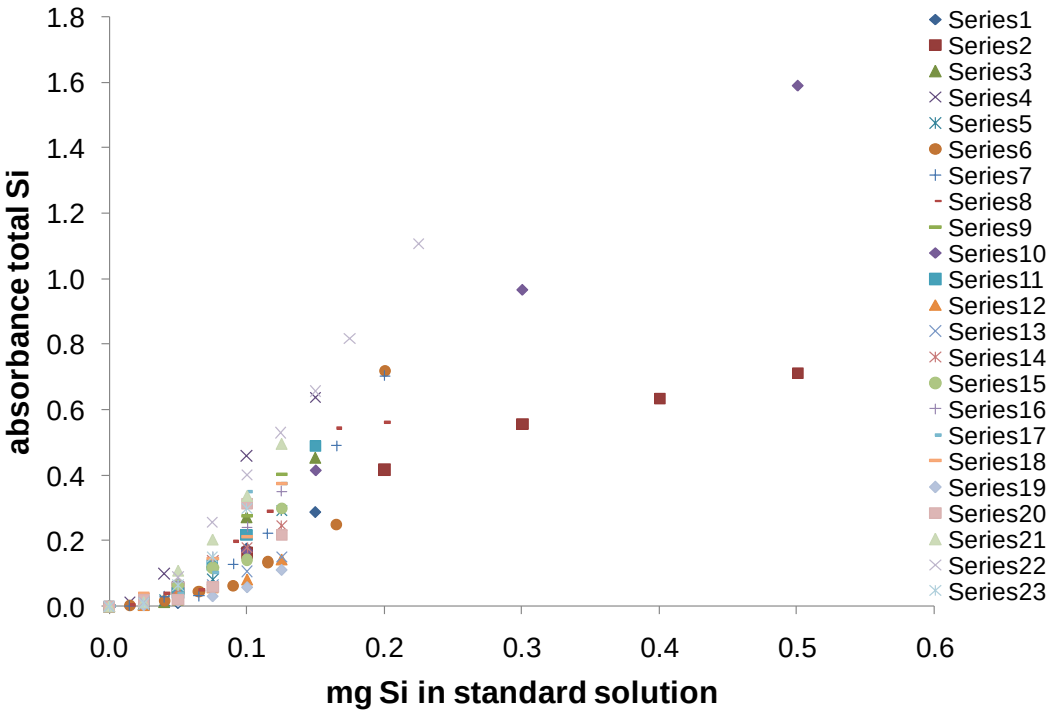


Figure 3.5: Absorbance of total Si measured in concentration series of twenty-three different standard solutions

It seems that the molybdenum blue method as described by Leroy (1998) and performed in this research is not fully suitable to detect Si in wood, especially when organosilicon compounds are added to the wood. Although direct alkali fusion is used before to detect Si in organosilicon compounds (McHard et al. 1948), Wetters and Smith (1969) pointed at the importance of the kind of alkali used. They found improved silicon recovery using potassium hydroxide rather than sodium hydroxide. Moreover the losses of volatile compounds and polymer rearrangement could be minimised when an alcoholic alkali pre-treatment step was performed. However, they state that silicon from linear polydimethylsiloxanes with molecular weights below that of octamethylpentasiloxane was not held sufficiently for quantitative use.

This study showed that quantitative determination of Si inside wood using the molybdenum blue method is not yet optimised. Knowing that no other methods are available, this leaves a gap for process optimisation and quality control of organosilicon treated wood. This lacking knowledge is however not restricted to this kind of wood treatments and is present also in the wood preservation and

wood modification area. It is therefore necessary to use product retention as basis for the determination of amounts of product applied to the wood.

3.4 Conclusion

Although the heteropoly blue method is often used to detect Si in both organic and inorganic samples, the detection of total Si present in organosilicon treated wood does not seem straightforward. The importance of the first decomposition step of the material, transforming the organosilicons to silicic acids is demonstrated again in this research. Further fundamental research about the exact transforming steps is necessary in improving the method for Si determination in organosilicon treated wood. Suggestions for further research are experimenting with different alkali fusions, preferably in combination with appropriate alcoholic pre-treatment. However, it remains questionable if high recovery rates can be achieved with low molecular weight linear and cyclic polydimethylsiloxanes, like the ones used in this research. Awaiting this further research precaution should be taken when using the existing molybdenum blue method or when citing values obtained in that way since they might be underestimating the real presence of Si in the sample.

Discussion

Both scanning techniques using SEM-EDX or micro-CT proved to be suited for the detection of organosilicons in treated wood. Their combination yielded even more information about the exact location of the applied products. This technique is therefore able to, when the products were doped prior to application, distinguish between superficial treatments like dipping and impregnation application based on the localisation of the organosilicons in the wood.

However, when more information is needed about the exact amounts of organosilicon present in the wood for i.e. quality control, the molybdenum blue method as presently available is less suited. The main problem is the first step of the analysis, namely transforming the organic Si into inorganic, soluble Si, which is more easily detectable. It is therefore necessary to fall back on the determination of product retention during treatment of the wood to have an idea of the loadings obtained due to treatment.

That is why further on in this research no use is made of the quantitative determination of Si using the heteropoly blue method. Instead specimens were always weighed before and after application as to determine the product retention, whether recalculated to weight percent gain or not. This method is also well known and used in the wood preservatives and wood modification areas and is therefore more practical, reliable and relevant to the industrial producers.

PART II

LABORATORY ASSESSMENT OF THE EFFICACY AND IMPACT OF ORGANOSILICON TREATMENTS ON WOOD

Preface

Trees are growing by a natural process using specific elemental substances. Each year they grow, become higher and wider and some extra wood is formed. However, they are only part of a big cycle of elements and energy and after their lifetime they will be broken down to elemental substances again, which are the basis for new life cycles. These processes are a main advantage of wood: it is a 100 % pure natural material and it will be broken down or decayed and recycled by nature itself.

However, when humans intervene in this cycle and use wood for their own purposes, the natural cycle does not stop. This means that wood will still be vulnerable to decay. While at the one hand this is exactly what we expect to happen with the wood once it has reached its useful end of life, we do not want it to happen during usage of the wood. Uniting these two contradictory expectations of wood is a challenge to everyone involved in the wood sector.

While we can prolong the service life of wood by selecting species combined with adequate design for each specific application, humans have searched and are still searching for ways to protect wood. The easiest way is using wood which is durable by its own, i.e. certain tropical wood species. However, most indigenous trees of temperate and boreal regions are not durable by their own and need extra protection. Therefore people have treated wood with biocides. Recent concerns of public and environmental health and disposal of the treated wood at the end of its service life has made some become opposed to the use of preservative treated wood and created the necessity to find less harmful preservatives. More recently efforts were undertaken to modify the properties of wood fundamentally to prolong its service life. Therefore a broad range of techniques has been applied and new developments are still on their way.

Whatever way of protecting the wood, something is added or changed, which is not naturally present there. Therefore the risk exists that certain components may leach out from this wood and come available in nature. This unmentioned availability of not natural components in nature could pose a certain threat to organisms somewhere in the big web of living organisms.

To be able to evaluate and compare wood products in a uniform way, standardized methods were developed, in that way creating criteria for products and treatment techniques. However, standards can only be developed after a new technique has come into existence. It is therefore interesting to question whether the existing methodologies evaluating efficacy and ecotoxicology of

(treated) wood can be applied just like that to wood treated with products belonging to a new product group, like organosilicons.

It was found necessary to determine how vulnerable organosilicon treated wood was to wood destroying organisms, and which methodology was best fitted for this purpose. Furthermore research was performed looking for a method combining the effective protection of wood without potentially harming other living organisms. Known wood treatments like wood preservation and wood modification were taken as a case study. Subsequently this method was applied to organosilicon treated wood and used to evaluate the leaching risk of organosilicon and biocide treated wood.

4 FUNGAL DECAY RESISTANCE AND DURABILITY OF ORGANOSILICON TREATED WOOD[1]

Abstract

The potential use of organosilicons as protective agents against basidiomycetes attack of wood used in outdoor applications was investigated using Scots pine sapwood and beech specimens. Both mini-blocks and EN 113 specimens were subjected to brown-rot and white-rot fungi. A dose-response could be observed showing that with higher weight percentage gain of the organosilicon, the resistance (i.e. efficacy) against fungi increased. At relatively low weight percentage gains, which are assumed to be economically feasible, Scots pine could be partly protected against decay by *Postia placenta* and *Coniophora puteana* and beech could be partly protected against decay by *C. puteana* and *Trametes versicolor*. Full protection was achieved by some silicones for Scots pine sapwood against *C. puteana* and for beech against *T. versicolor*. The most promising products were a solvent-based mixture of the alkoxysilanes methyltrimethoxysilane (MTM) and octyltriethoxysilane (OTES) and a water-based micro-emulsion of polydimethylsiloxane (PDMS) and triethoxysilane (TES) when applied above 20 and 30 % weight gain for Scots pine and above 30 and 40 % weight gain for beech. A water-based mixture of dimethylmethylhydrogen siloxane (DMS) and N-octyltriethoxysilane (n-OTES) was able to protect beech at weight gains above 30 %.

[1] Published as:
De Vetter, L., Stevens, M. and Van Acker, J. 2009. Fungal decay resistance and durability of organosilicon-treated wood. International Biodeterioration and Biodegradation. 63: 130-134.

4.1 Introduction

Wood is a natural material that is subject to biological degradation. To keep the wood in optimal condition as long as possible, proper protection and/or preservation of wood is pursued, and a broad range of chemicals may be used. Recent environmental concerns about the toxicity and persistence of some preservative products have stimulated researchers to find alternatives (Hill et al. 2004; Mai and Militz 2004b; De Vetter et al. 2006). Modifying wood is an often-followed route. More precisely, modification using non-biocidal thermal, chemical or resin treatments shows potential to improve wood characteristics (Kamdem et al. 2002; Lande et al. 2004b; Hakkou et al. 2006).

Since organosilicon compounds such as silanes and siloxanes have been shown to protect masonry, textiles, ceramics, etc. (Rochow 1987; Ren and Kagie 1995; Mayer 1998) their suitability to protect wood was investigated. Although these chemicals owe their effectiveness mainly to their hydrophobicity, several trials were undertaken to evaluate the effectiveness of these products in protecting wood against fungal decay. The idea is that by reducing the moisture content of wood, fungal growth is prohibited. Both encouraging and discouraging results have been reported (Goethals and Stevens 1994; Donath et al. 2004, 2006b; Hill et al. 2004; Mai and Militz 2004b; Mai et al. 2005).

The objective of this research was to assess the effectiveness of a range of silicones as a function of their weight percentage gain. Secondly, the efficacy of these products at economically feasible retention levels was evaluated. An important aspect of this research is the way the results and more precisely the mass losses are interpreted. Not only the mass losses as such, but also the corresponding natural durability levels are considered to be important factors in the evaluation of a treatment. Focus is put on outside, above-ground application, since this is the type of use where organosilicons have the most potential to be applied effectively.

4.2 Materials and methods

4.2.1 Treatment of specimens

One of the main purposes of this research was to evaluate silicones in a concentration range as broad as possible. Therefore the water-based organosilicons W1, W2, W4 and W5 and both solvent-based organosilicons S1 and S2 were selected (Heading 1.3.1). For all products except W4, a concentration series of four dilutions was made. Demineralised water was used to dilute the water-based products and isopropyl alcohol to dilute the solvent-based products.

All specimens were impregnated according to the requirements of EN 113 (1996) as explained under 1.3.2. The WPGs were recalculated to active ingredient retention (kg/m³) in the wood using the average volumetric masses, which were 545 kg/m³ for Scots pine sapwood and 731 kg/m³ for beech.
Since the focus of the experiment was to evaluate performance of the treated blocks for use class 3 applications, the effect of ageing of the blocks on fungal resistance was investigated. Therefore it was decided to leach the specimens of one specific test according to European Standard EN 84 as provided in EN 599 (1996) for outdoor applications. The samples were first impregnated with water in the same way as described under heading 1.3.2. Subsequently the leaching water was decanted and replaced nine times over a period of 14 days using a wood/water volume ratio of 1/5. The specimens were dried afterwards, first under ambient conditions and then at 60 °C.

4.2.2 Test methodology

In a first test set-up concentration ranges of different types of silicones were evaluated (test 1). These ranges varied in active ingredient content between 5 and 50 Wt %, depending on the product. Small, so-called mini-block specimens of 5 × 10 × 30 mm (R × T × L) of Scots pine sapwood (*Pinus sylvestris* L.) and

beech (*Fagus sylvatica* L.) were used. Since Bravery (1978) showed toxic values obtained with such mini-blocks after 6 weeks incubation were comparable with those obtained after 12 weeks using sample sizes described in EN 113 (1996), the specimens were exposed to the fungi only half as long (8 weeks) as prescribed in the standard (EN 113; 16 weeks).

In a second test (test 2) Scots pine sapwood and beech specimens with standard dimensions 15 × 25 × 50 mm (R × T × L) were treated at approximately 0.5 and 2.5 Wt % active ingredient content and subsequently exposed to the fungi according to the combined procedures of the European Standards EN 113 and CEN/TS 15083-1 (2006).

To assess the impact of leaching on the protective effectiveness of silicones against wood degradation, a third test (test 3) was performed. Scots pine sapwood specimens similar to test 2 were, after treatment at 5 Wt % active ingredient content and prior to fungal exposure, subjected to leaching according to European Standard EN 84 (1996). For all three test set-ups six replicates per treatment were used.

4.2.3 Decay resistance testing

For all three tests the decay resistance was assessed based on the procedures described in the European Standards EN 113 and CEN/TS 15083-1 (Table 4.1). After treatment (or after subsequent leaching) the specimens were γ-sterilised. Kolle flasks containing 3 % malt agar extract culture medium were inoculated with one of the following fungi: *Coniophora puteana* (Schumach.) P. Karst (strain BAM ebw. 15) or *Postia placenta* (Fr.) M.J. Larsen & Lombard (syn. *Poria placenta* (Fr.) Cooke, strain FPRL 280) for Scots pine sapwood and *C. puteana* or *Trametes versicolor* (L.) Lloyd (syn. *Coriolus versicolor* (L.) Quél., strain CTB 863 A) for beech. Subsequently both a treated and an untreated control specimen were aseptically introduced into each flask onto a sterile test specimen support. For the mini-block test the exposure to the fungi differed somewhat. Into each Kolle flask all four specimens of a concentration range plus two untreated control specimens were introduced. Untreated control

specimens were put in separate Kolle flasks to test virulence of the fungi. Extra silicone-treated (and leached) specimens were used to determine a correction value C, of the variations in mass of the treated specimens resulting from factors other than attack by the test fungi. The mini-blocks were exposed for only 8 weeks, whereas the specimens of tests 2 and 3 were subjected to fungal attack for 16 weeks, as stipulated in the standards. At the end of the exposure time adhering mycelia were removed from the specimens and, after weighing, they were oven-dried at 103 °C and reweighed (m_{dry}). These masses allowed calculating the mass loss (ML, Eq. 4.1) of each specimen.

$$ML\ (\%) = \left[\frac{m_{untreated} - m_{dry}}{m_{untreated}} \times 100\right] - C \qquad (4.1)$$

Table 4.1: Durability rating scale according to CEN/TS 15083-1

Durability class	Description	Median mass loss (%)
1	Very durable	≤ 5
2	Durable	> 5 to ≤ 10
3	Moderately durable	> 10 to ≤ 15
4	Slightly durable	> 15 to ≤ 30
5	Not durable	> 30

4.3 Results

4.3.1 Silicone uptake

Figures 4.1 and 4.2 summarize the WPGs and their corresponding retention levels of active ingredients after impregnation into Scots pine sapwood and beech specimens. As stated in De Vetter and Van Acker (2005) the difference in sample size between mini-blocks and EN 113 specimens did not have a major influence on the WPG. The calculated WPGs based on solution uptake were similar for all water-based treatments (circa 8 %) and for all solvent-based treatments (circa 6 %) when impregnated with a 5 Wt % active ingredient concentration. The average WPG for all Scots pine sapwood impregnations was

approximately 30 % higher than the one for beech. This corresponds well with results reported by Goethals and Stevens (1994).

Test 3 specimens were dried at 60 °C both prior to impregnation and afterwards. These masses made it possible to calculate an alternative weight percentage gain after curing. The recorded value is in general slightly higher than the calculated WPG based on solution uptake, although no significant trends can be determined when the standard deviations are taken into account (Figure 4.3). The strikingly higher weight gain of S2 and S1 might be attributed to the solvents which were not fully removed from the specimens at 60 °C. After the leaching procedure, the specimens were again dried at 60 °C until constant mass was reached, allowing calculation of yet another WPG. These last WPGs were a lot lower than the previous WPGs, indicating potential loss of product and wood constituents due to leaching.

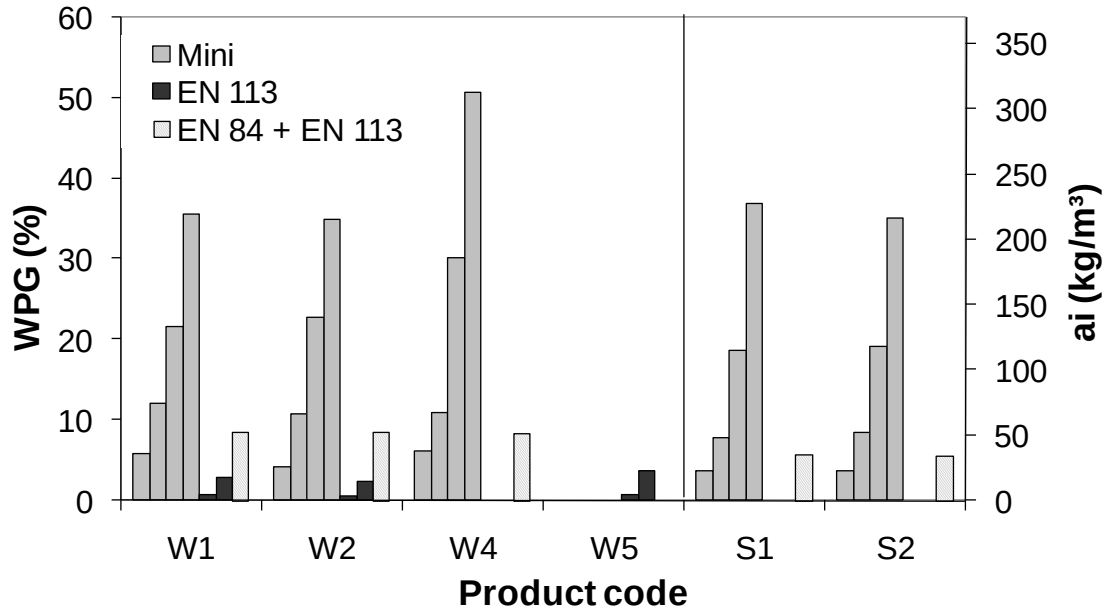


Figure 4.1: Weight percent gain (WPG) and corresponding retention of active ingredient (ai) of all organosilicons used to impregnate Scots pine sapwood specimens for usage in a mini-block test, a standard EN 113 test and an EN 113 test preceded by EN 84 leaching

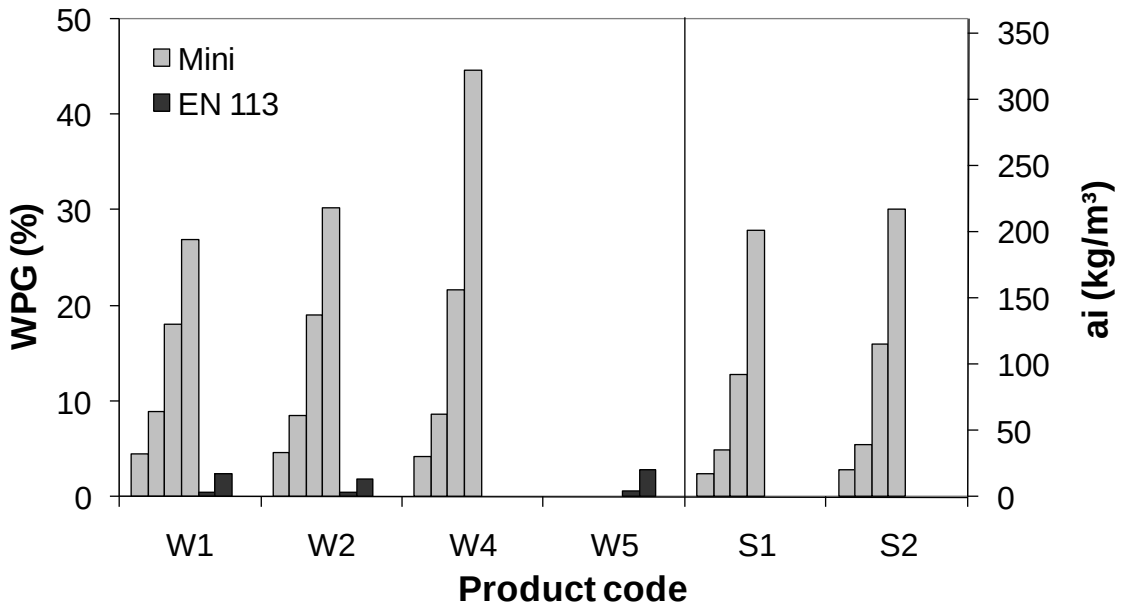


Figure 4.2: Weight percent gain (WPG) and corresponding retention of active ingredient (ai) of all organosilicons used to impregnate beech specimens for usage in a mini-block test, a standard EN 113 test and an EN 113 test preceded by EN 84 leaching

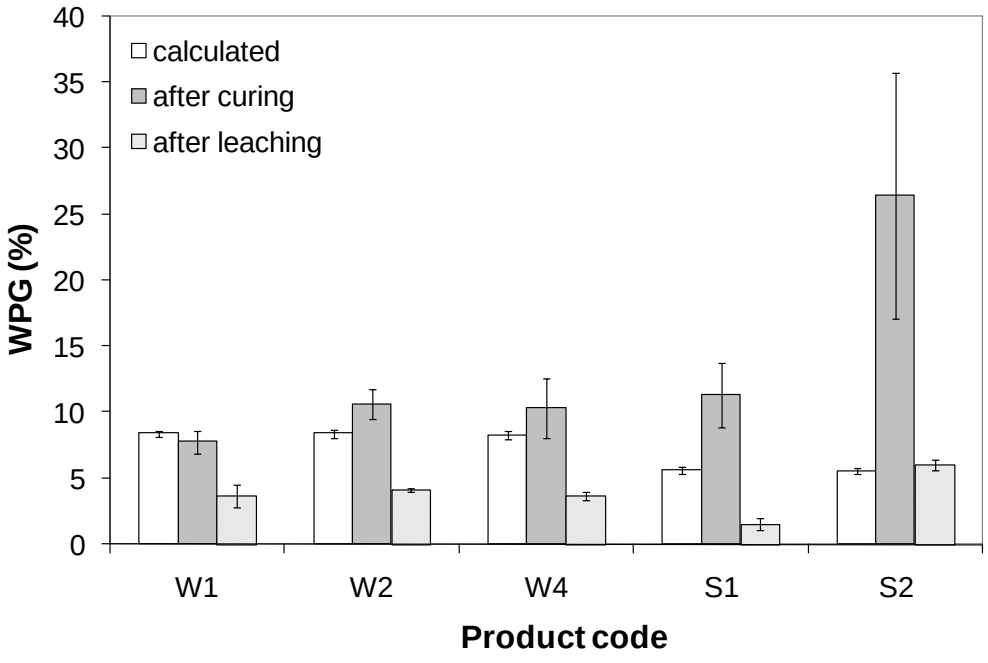


Figure 4.3: WPG of Scots pine EN 113 specimens impregnated with 5 % active ingredient concentrations of different organosilicons and leached according to EN 84

4.3.2 Resistance to fungal decay of silicone-treated wood in relation to WPG

The mini-block test (test 1) was performed as a screening procedure to look for a dose-response curve between WPG and mass loss of the specimens. During the test Scots pine sapwood was exposed to the brown-rot fungus *C. puteana*, and beech was exposed to the white-rot fungus *T. versicolor*. In line with the conclusions of Smith and Orsler (1994) showing that the use of median mass loss eliminates the impact of shootouts, this value was preferred over the mean value. The resulting graphs are shown in Figures 4.4 and 4.5 for Scots pine sapwood and beech, respectively.

Figure 4.4 clearly shows a dose-response curve between WPG and mass loss for Scots pine sapwood after 8 weeks exposure to *C. puteana*. While at low WPGs the mass losses of W1 and S1 treated wood do not differ significantly from the mass loss of untreated Scots pine sapwood (60 %), the other products manage to reduce the mass loss. All mass losses decreased with increasing WPGs. To what extent seems to depend mainly on the product applied. Products W1 and S2 have a sharp drop in mass loss in function of WPG, whereas for products W2 and S1 the slope of this function is gentle. Different evaluation criteria may be used. For example, when the wood preservatives approach is used, the limit for full protection is set at 3 % mass loss (EN 599 1996). Only products W4 and S2 succeeded in reaching this limit and this was at WPGs of approximately 30 % and 20 %, respectively.

If the durability approach is adopted (CEN/TS 15083-1 2006) then the mass losses obtained are attributed to a durability class according to the criteria given in Table 4.1. The resulting classes are included in Figure 4.4, which shows that at low WPGs product W4 is able to induce an improvement in durability with one class. With increasing WPG, all products, except for W2 and S1, are able to induce an additional improvement in durability class of three to four classes. However, in this study the emphasis was on application in use at the class 3

level, meaning that products S2, W4, and W1 can protect the wood adequately at WPGs of approximately 15 %, 20 %, and 30 %, respectively.

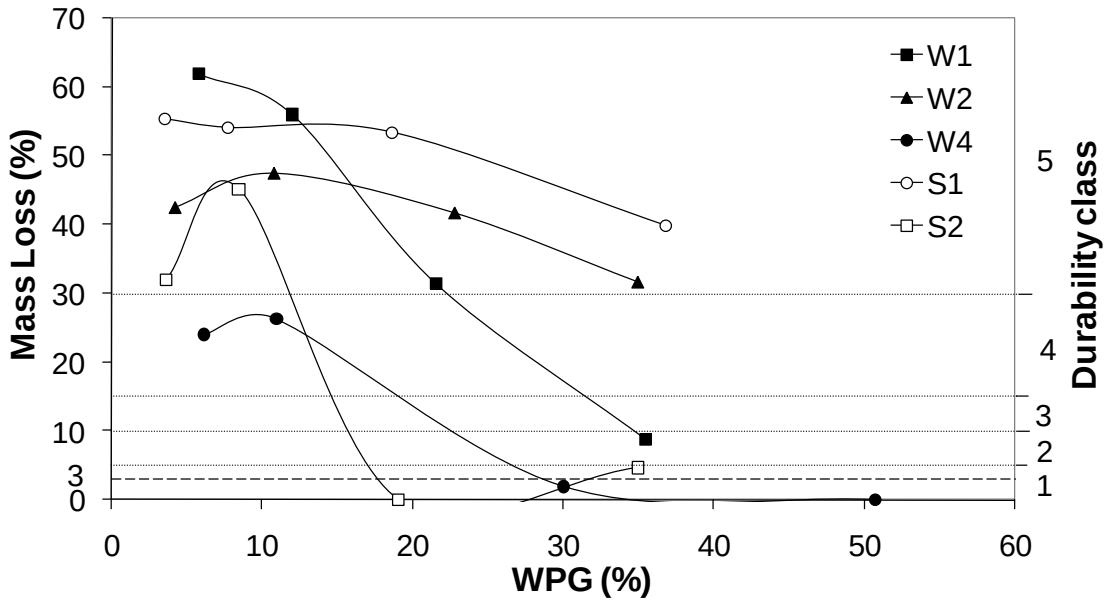


Figure 4.4: Median mass loss and durability class in relation to WPG for silicone-treated Scots pine mini-blocks exposed to *Coniophora puteana* during 8 weeks

The gradients of the dose-response curves of treated beech are comparable with each other irrespective of the product applied, except for product S1, which has a steep slope at WPGs lower than circa 15 %, after which a plateau is reached (Figure 4.5). Product W2, by contrast, generates a fast decrease in mass loss at WPGs above 20 %. If the wood preservatives approach is used to analyse the mass losses, more than half of the products achieve a mass loss below the 3 % limit when applied at WPGs in excess of circa 30 % (W2 and S2) or circa 40 % (W4). The natural durability approach would classify untreated beech exposed to *T. versicolor* as class 4 based on a median mass loss of 25 % after 8 weeks of exposure. Usually untreated beech is classified in durability class 5 (EN 350-2 1994), indicating that a longer exposure in this test set-up might have been useful. None of the products applied at low WPGs induced an improvement in durability class for beech compared to untreated beech, whereas product W4 could do so for Scots pine sapwood. Nevertheless, with increasing WPGs, improvements in durability up to four classes can be

achieved. Referring to application in use class 3, products S2, S1, W4, and W2 can protect beech sufficiently at WPGs in excess of approximately 8, 15, 20, and 25 %, respectively.

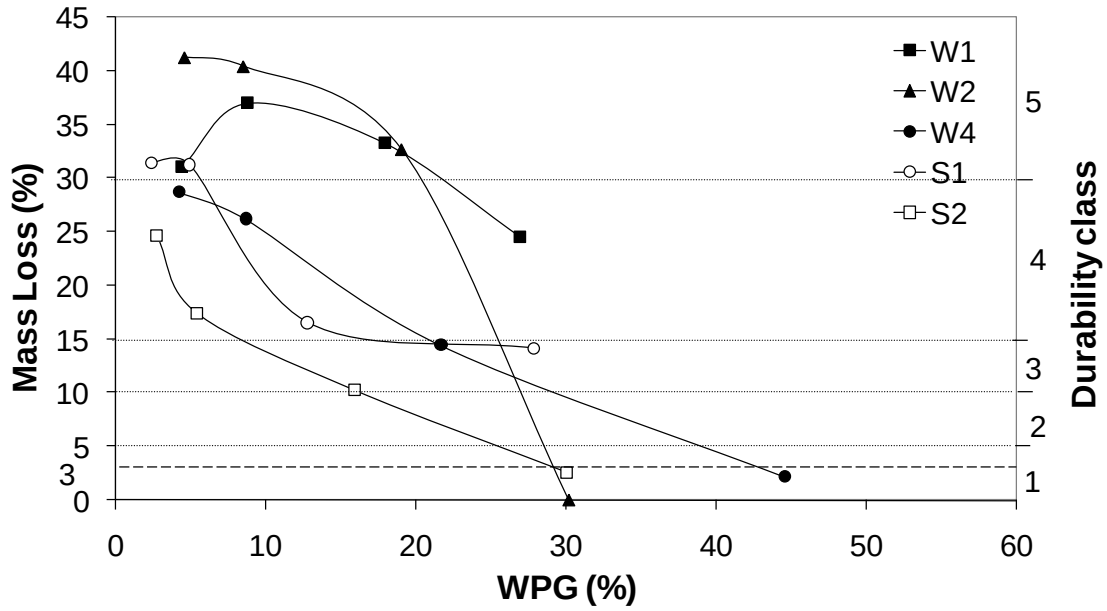


Figure 4.5: Median mass loss and durability class in relation to WPG for silicone-treated beech mini-blocks exposed to *Trametes versicolor* during 8 weeks

4.3.3 Resistance of wood treated at low silicone WPG concentrations against wood-rotting fungi

Since the higher WPGs are not considered to be economically feasible and the test results reported above indicated that at low WPGs the products have an influence on the biological durability of Scots pine sapwood and beech, focus was put on treatments achieving lower WPGs. This second, in-depth investigation was performed according to the recommendations of Van Acker et al. (2003). Scots pine sapwood EN 113 specimens were exposed to *C. puteana* and *P. placenta* and beech specimens to *C. puteana* and *T. versicolor*. In contrast to the broader initial study, this research concentrated on three water-based organosilicons applied at two very low concentrations between 0.4 (2.3 kg/m³) and 3.6 % (17.5 kg/m³) WPG (ai). Table 4.2 gives the exact WPGs, the corresponding mass losses, and durability classes obtained for unleached

Scots pine sapwood and beech specimens after 16 weeks exposure. Noteworthy is the much lower mass loss observed for untreated Scots pine sapwood EN 113 specimens compared to the corresponding mini-block specimens when exposed to *C. puteana*. This suggests no full correspondence between 16 weeks standard EN 113 exposure and 8 weeks mini-block exposure of Scots pine sapwood to *C. puteana*.

Table 4.2: WPG (%), median ML (%) and DC of untreated and organosilicon-treated EN 113 specimens after 16 weeks exposure to wood-rotting fungi

Treatment	Scots pine sapwood					Beech				
	WPG	*C. puteana*		*P. placenta*		WPG	*C. puteana*		*T. versicolor*	
		ML	DC	ML	DC		ML	DC	ML	DC
Untreated	-	41.4	5	28.4	4	-	47.4	5	28.0	4
W1	0.6	33.8	5	30.3	5	0.5	43.3	5	34.9	5
	2.8	49.2	5	29.1	4	2.3	47.6	5	36.8	5
W2	0.5	19.7	4	27.2	4	0.4	49.9	5	nd	nd
	2.3	18.7	4	31.2	5	1.9	41.6	5	nd	nd
W5	0.7	35.8	5	32.8	5	0.5	39.1	5	35.9	5
	3.6	34.0	5	26.4	4	2.8	43.3	5	39.8	5

nd: Not determined

Although the specimens in the second EN 113 test were treated at a lower concentration than those of the first mini-block test, extrapolation of the dose-response curves shows that the median mass losses of W1 and W2 treated Scots pine EN 113 specimens are a lot lower than the losses of the corresponding mini-block specimens, at comparable WPGs. For beech, the median mass losses of untreated and W1 treated EN 113 specimens after 16 weeks exposure to *T. versicolor* are comparable to the median mass losses of mini-blocks after 8 weeks of exposure. Notwithstanding the generally lower mass losses of the EN 113 specimens, none of the products can protect the wood sufficiently against fungal attack according to the wood preservatives' approach.

Concerning the durability approach, only product W2 can induce an improvement in durability class of Scots pine. However, since the highest median mass loss for all test fungi obtained for a certain wood species must be

considered to determine the natural durability of the wood species, treated Scots pine and beech are considered not durable (class 5). Although generally disappointing, the test shows that silicones may have an effect on the resistance of wood against fungi, yet it is confirmed again that higher concentrations and/or retentions are required.

This brought about the third test reported here, at a slightly higher concentration than was used before (5.6 to 8.4 % WPG, 27.9 to 37.3 kg/m³ ai). Scots pine sapwood was impregnated with the three water-based and two solvent-based products as applied in the first test set-up. To see if there is any leaching effect, the specimens were subsequently leached according to European Standard EN 84. After drying, the standardized specimens were exposed to *C. puteana* for 16 weeks. The mass losses of the (un)treated wood and the corresponding durability classes were determined (Table 4.3).

Table 4.3: WPG (%), median ML (%) and DC of untreated and organosilicon treated EN 113 specimens after EN 84 leaching and exposure to *C. puteana* during 16 weeks

Treatment	WPG (%)	ML (%)	DC
Untreated	-	31.7	5
W1	8.6	35.3	5
W2	8.6	26.0	4
W4	8.4	10.9	3
S1	5.7	35.8	5
S2	5.7	19.3	4

Again the recorded mass losses of the EN 113 specimens after EN 84 leaching are considerably lower than the mass losses of the corresponding mini-blocks when exposed to *C. puteana*. Contrary to the previous test, the slightly higher WPGs can now significantly improve the durability class. Products W2 and S2 may induce an improvement of one durability class, whereas product W4 is even able to improve the wood by two durability classes. In fact this means that even after leaching, Scots pine sapwood treated with product W4 is still moderately durable (durability class 3). Also Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco) and tropical wood species such as Sapelli (*Entandrophragma*

cylindricum Sprague), Movingui (*Distemonanthus bethamianus* Baill.) and Piquia (*Caryocar* spp.) belong to this class, which allows as such usage for exterior joinery.

4.4 Discussion and conclusion

Published results report different effects for organosilicons used for wood protection. Hill et al. (2004) found that treatment of Corsican pine sapwood (*Pinus nigra*) with vinyltrimethoxysilane (VTMS) reduced the mass loss due to decay by *C. puteana* only slightly, even at WPGs in excess of 45 %. When Corsican pine was treated with [γ-(methacryloxy)propyl]trimethoxysilane (PTMS) and exposed to *C. puteana*, the dose-response line indicated that full protection may occur at WPGs in excess of 80 %. For exposure to *T. versicolor*, the toxic threshold for decay resistance was found at circa 40 % WPG for both VTMS and PTMS treated wood. Goethals and Stevens (1994) confirmed that PTMS treated Scots pine sapwood (3 to 22 % WPG) did not show any significant protection against *C. puteana*. The authors also found that PTMS treated beech (2.75 to 14 % WPG) was poorly protected against *T. versicolor*. Donath et al. (2004) reported that beech could be protected against *T. versicolor* when treated with tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and propyltriethoxysilane (PTEO) as monomeric silane or as pre-hydrolysed sol. The lowest mass loss was observed with samples treated with MTES and PTEO (silane treatment, 11 and 14 % WPG). According to the European Standard CEN/TS 15083-1, these samples are to be classified as very durable (class 1). The corresponding sol treatments led to durability classes 2 (PTEO, 15 % WPG) and 3 (MTES, 13 % WPG). They also put forward that alkoxysilanes caused a delay of fungal attack, indicating that after longer exposure time heavy decay occurred. Mai et al. (2005) reported good decay resistance of Scots pine sapwood and beech treated with oligomeric silane systems containing aminosilanes. Treated Scots pine mini-blocks were fully protected at 16 % WPG against *C. puteana* over an exposure time of 18

weeks. In contrast, treated beech mini-blocks (11 % WPG) resisted decay by *T. versicolor* only during the first 6 weeks of exposure.

The results of the present study showed an increased decay resistance with increased WPG for all organosilicon formulations. Remarkable for Scots pine and beech is the observation that both water-based and solvent-based formulations can protect the wood equally well at comparable WPGs. The solvent-based MTM/n-OTES (S2) and the water-based micro-emulsion PDMS/TES (W4) could protect Scots pine sapwood against *C. puteana*, just like the oligomeric silane system used by Mai et al. (2005). They found that the oligomeric silane system caused a higher reduction in the decay rate than did alkylsilanes at similar WPGs and that this may be attributed to the amino groups in the oligomer. In this research for the alkoxysilanes of S2 a comparable WPG of circa 20 % was needed, whereas a higher WPG of circa 30 % was necessary for the siloxane/silane mixture (W4) to protect the wood sufficiently. Both products were also able to protect beech from degradation by *T. versicolor* at WPGs in excess of 30 and 40 %, respectively. Also the mixture of DMS and n-OTES (W2) proved to be effective for beech against *T. versicolor* when applied above circa 30 % WPG. These WPGs are a lot higher than those reported by Donath et al. (2004) and Mai et al. (2005) for silane systems after 6 weeks of exposure, although full protection was not reached.

The other products applied in this research cannot protect the wood sufficiently at the concentrations at which they were applied. Nevertheless, for some of them, higher retention values might generate sufficient protection. The effectiveness of the WPGs shown in this research corresponded with high active ingredient concentrations (at least 25 %), which do not seem economically feasible as alternatives for traditional wood preservation methods. In fact even application at 5 Wt % active ingredient seems economically feasible only when performed with solvent-based products. Their water-based counterparts are more costly.

If the treated specimens are considered as a new wood species, they could be evaluated according to the natural durability approach (EN 350-1). This seems to be a more logical approach, since silicones are no preservatives, nor is their application a chemical modification of the wood in a strict sense (De Vetter and Van Acker 2005). Focusing on class 3 use, the natural durability of Scots pine sapwood and beech would need to be improved by two classes. Depending on the test method applied, the 40 Wt % mixture of DMS and n-OTES (W4) succeeded in doing this for Scots pine sapwood at circa 20 % (mini-block test) or circa 8 % (EN 113 test after EN 84 leaching) WPG. This big difference in WPG seems at first sight strange. However, in the mini-block test untreated Scots pine sapwood had a mass loss of circa 60 % after 8 weeks, whereas this mass loss amounted to circa 30 % in the EN 113 test with EN 84 leaching after 16 weeks of exposure. Taking the ratio of mass loss of the untreated specimens into account, the discrepancy in WPG corresponding with durability class 3 between the different test set-ups no longer seems inexplicable. Aside from product W4, the 100 Wt % MTM/ n-OTES (S2) and the 50 Wt % DMS/n-OTES (W1) can enhance the natural durability of Scots pine sapwood to durability class 3 when applied at circa 15 and 30 % WPG (mini-block test), respectively.

For beech all organosilicons, except for one, can adequately protect the wood when used outdoors not in ground contact. Although the exact WPGs at which organosilicons improve the natural durability to class 3 may be under discussion, the authors want to stress that regardless of the testing procedure, organosilicons show potential in improving the natural durability of Scots pine sapwood and beech. They might be a valuable component of more complex formulations aiming at protecting wood from fungal decay under outdoor conditions out of ground contact, as has been proposed before (Mai and Militz 2004b; Donath et al. 2006a).

The conclusions of the wood preservation tests for Scots pine sapwood and beech are that they can be protected effectively against fungal attack, but only at high WPGs. Both water-based and solvent-based products qualify for this

purpose. Among the water-based products the 100 % active micro-emulsion seemed the most promising. By focusing on applications such as exterior, above-ground use, that requires wood with a biological durability equivalent to natural durability class 3, the use of organosilicon treatments is even more likely to have potential, especially when part of more complex formulations.

Acknowledgements

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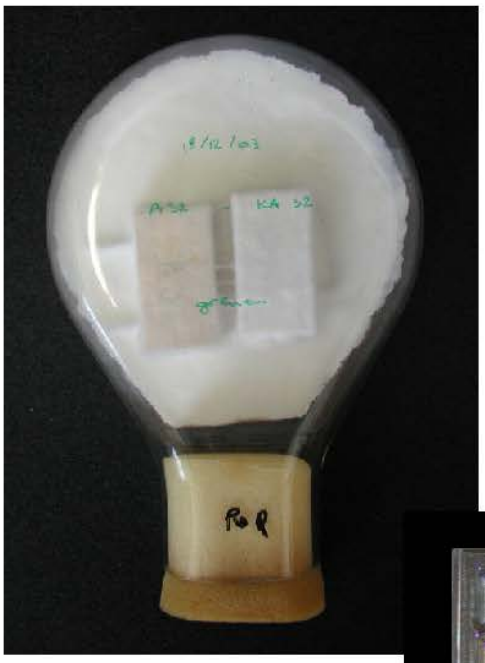

5 METHODOLOGY TO ASSESS BOTH THE EFFICACY AND ECOTOXICITY OF PRESERVATIVE TREATED AND MODIFIED WOOD[1]

Abstract

Wood used in outdoor conditions out of ground contact is susceptible to weathering, inducing both fungal decay and leaching of components to the environment. This paper presents a methodology to determine these two parameters for untreated, preservative treated and modified wood. Therefore the wood was first leached and subsequently exposed to fungal decay of the most prominent wood rotting fungi. The crustacean *Daphnia magna* was exposed to the leachates to provide information on their impact on the environment. Combining both parameters reveals that preservative treated wood and modified wood are capable of protecting the wood adequately for application under use class 3 conditions without putting a threat to the environment. This proves the suitability of the concept of combining efficacy and ecotoxicity for the evaluation of new type wood treatments.

[1] Published as:
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5.1 Introduction

Wood is a very valuable material which is rather cheap, easy to process, has good strength properties and an aesthetic appeal. Due to the numerous wood species lots of combinations of these properties are available. That is why wood is in demand as building material, both for interior applications as well as outdoor end uses. For wood in exterior applications out of ground contact (use class 3) enhanced wood properties are needed to prevent fungal deterioration. To resolve this problem both wood preservation using biocides and non-biocidal strategies can be envisaged. Since these exterior applications are susceptible to weathering some components may leach from the wood, regardless the strategy used to protect it. This way these components come available in nature and may pose a threat to the environment. Therefore, when evaluating new products both the efficacy against fungi, basidiomycetes in particular, as well as the ecotoxicological profile are important. This is also in line with the intention of the European Biocidal Products Directive (1998). Up to now no overall approach exists to combine these two important evaluation criteria. The purpose of this paper is to elaborate on methodology to determine and combine these two parameters.

One of the most used heavy duty wood preservatives in the biocidal strategy is CCA (salts of copper, chromium and arsenic). However, in several European countries and the USA this product is subjected to limitations concerning the production, trade and use of it (Hingston et al. 2001; Lande et al. 2004a; Donath et al. 2006b). Meanwhile optimised alternatives for CCA are on the market. Closest to CCA are other copper-based products which combine copper with organic molecules such as azoles, amines, quat (alkaline copper quaternary ammonium salts) and HDO (bis[N-cyclohexyldiazeniumdioxy] copper) (Cowan and Banerjee 2005). Common to all preservatives is that their toxicity to fungi is dependent on their mode of action (Lande et al. 2004a). Major disadvantage of the broad spectrum Cu-based wood preservatives is their susceptibility to

leaching inducing a subsequent potentially high ecotoxicity (Townsend et al. 2005).

In the non-biocidal protection strategy it is not the purpose to add a compound to the wood which is toxic to degrading organisms, but to change the chemical structure of the wood in such a way that it becomes unattractive/unrecognizable to micro-organisms. Another way is to lower the fiber saturation point of the wood below the minimal moisture content of the wood necessary for fungal degradation (Boonstra et al. 1998). Since the primary purpose of most wood modification techniques is to improve properties of the wood such as dimensional stability, hydrophobicity, fire retardance, mechanical properties, aesthetic appearance of the wood but also its resistance to wood deterioration they can be an alternative for the more traditional preservative treatments of wood (Lande et al. 2004a; Tjeerdsma and Militz 2005). It is also the purpose to produce a material that can be disposed of at end of life without environmental hazard (Hill 2006).

In this paper so-called thermally and chemically/impregnation modified wood as defined by Hill (2006) are covered. More precisely thermally modified spruce according to the Plato-process is assessed (Plato International bv, the Netherlands). This two-step heat treatment consists of an initial hydrothermal treatment of the wood, followed by a drying step and finalised by curing, after which conditioning of the wood takes place (Boonstra et al. 1998; Lande et al. 2004a; Hill 2006; Boonstra et al. 2007). LCA studies commissioned by Plato Wood have shown that the product has superior environmental performance compared with materials such as concrete and PVC, as well as preservative treated wood products (creosote and CCA) (Hill 2006). Kamdem et al. (2000) reported already that both toxic and non-toxic compounds were formed during a one-step heat treatment. Due to the lack of quantification of these products they were not able to decide whether the final product was toxic or not. The durability of thermally modified wood and different hypotheses for the mechanisms are reported in several publications (Boonstra et al. 1998; Tjeerdsma et al. 1998;

Kamdem et al. 2002; Hakkou et al. 2006; Boonstra et al. 2007). It was shown that neither the increase of the hydrophobic character of the wood, nor the generation of new extractives during heat treatment are responsible for this increase in durability. In contrast to the degradation and/or modification of hemicelluloses, which are generally considered as an important nutritive source for the development of wood rotting fungi, the modification of the lignin network and changes of the external conditions affecting the microenvironment are thought to affect the decay mechanism of thermally modified wood increasing its resistance against fungal attack. They also stipulate that it is difficult to distinguish which heat treatment effect contributes to the improved resistance against fungal attack.

Besides this thermal modification also chemical modification and more specifically furfurylation was included. Both southern yellow pine (SYP) and maple were treated according to a process developed by Kebony asa (Norway), the so-called Kebony® treatment. SYP was also treated with the BioRez^{TM} solution, following a process developed by TransFurans Chemicals bvba (Belgium). The furfuryl alcohol (FA) of both the Kebony and BioRez solutions are derived from furfural originating from hydrolysed agricultural wastes. The Kebony treatment of wood consists of an impregnation with FA including additives using a full cell process, followed by a curing step at elevated temperatures to induce polymerization and ended by kiln drying of the wood (Lande et al 2004b). Besides grafting of the FA or polyfurfuryl alcohol to wood cell-wall polymers, also homopolymerization and copolymerization with additives or wood extractive substances take place during the process (Lande et al. 2004a).

Despite all the research efforts performed up to now it remains difficult to find a way to treat wood combining sufficient efficacy against fungal decay and provide an excellent ecotoxicological profile of the leachates at the same time. That is why the objective of this research was to find a methodology to evaluate wood for usage in outdoor applications without ground contact, taking both the

efficacy of the wood against fungal degradation as well as the ecotoxicity of the wood leachates into account. In a first attempt it was the purpose to include at the one hand the most abundant wood destroying fungi and on the other hand a fast, easy and low-cost evaluation of the ecotoxicity of the wood leachates. Therefore the resistance of preservative treated and modified wood to the basidiomycetes *Coniophora puteana*, *Postia placenta* and *Trametes versicolor* and the ecotoxicity of the wood leachates using *Daphnia magna* were evaluated. Since Waldron et al. (2003) already demonstrated the importance of the leaching procedure and in order to have a more general picture of the ecotoxicity in outdoor performance; two different leaching procedures were evaluated. In that respect it was preferred to include both a harsh as well as a mild leaching procedure. Also different harvesting times were considered.

5.2 Materials and methods

5.2.1 Materials

Reference wood species

Since treated wood is used to either benchmark or outperform other wood available, several reference wood species were included in the research. Both tropical and temperate wood species covering both softwood and hardwood species were used (Table 5.1). As native wood species oak, beech and Scots pine were chosen. Furthermore wood derived from the domesticated species Douglas fir and black locust were examined. Because of their high natural durability (Lincoln 1994; EN 599 1996) also the tropical wood species padauk, azobé, merbau and bangkirai were included. They exhibit an inherent toxicity due to the abundant presence of extractives in the wood. It is already proven that these extractives may leach out under laboratory conditions, using a variety of extraction methods (Hillis 1987; Van Eetvelde et al. 1998). As such these extractives may harm the environment. Two relatively new wood species on the European market originating from South America were added, namely abiurana

and piquia. All these tropical wood species are frequently used in water constructions such as canal lining and lock gates or in other outdoor applications such as exterior joinery, cladding, fencing and garden furniture, indicating they are suited to be used in use class 3 or even higher use classes. In these outdoor applications they may pose a potential hazard to the (aquatic) environment and are therefore examined in this test set-up.

Table 5.1: Overview of wood species used, their botanical name, origin and natural durability (Lincoln 1994)

Wood species	Botanical name	Origin	Natural durability (EN 350-2)
	Softwoods		
Scots pine sapwood	*Pinus sylvestris* L.	Europe, Asia	5
Scots pine heartwood	*Pinus sylvestris* L.	Europe, Asia	3-4
Douglas fir	*Pseudotsuga menziesii* (Mirb.) Franco	North America, Europe[1]	3
	Temperate hardwoods		
Beech	*Fagus sylvatica* L.	Europe	5
Oak	*Quercus robur* L. / *petraea* Lieblein	Europe, Asia	2-3
Black locust	*Robinia pseudoacacia* L.	North America, Europe[1]	1-2
	Tropical hardwoods		
Abiurana	*Pouteria guianensis* Aubl.	South America	1-2
Azobé	*Lophira alata* Banks ex Gaertn.f.	West Africa	1(-2)
Bangkirai	*Shorea laevis* Ridl.	Southeast Asia	2
Merbau	*Intsia bijuga* (Colebr.) Kuntze.	Southeast Asia	1-2
Padauk	*Pterocarpus soyauxii* Taubert	West Africa	1
Piquia	*Caryocar villosum* (Aubl.) Pers	Central America	2-3

[1] Domesticated in Europe (material used for this research)

Preservative treated wood

Scots pine sapwood was treated with different wood preservatives that are on the market for heavy duty application, mainly copper-based wood preservatives. In this respect CCA (copper, chromium, arsenic salt) was the reference wood

preservative (Tanalith CO, Arch Timber Protection nv, Belgium; 30.6 % CrO_3, 11.1 % CuO, 17.3 % As_2O_5), and three other Cu-based wood preservatives were included, namely a Cu-amine (Impralit KDS, Rütgers Organic Gmbh, Germany; 20.5 % $CuCO_3$-$Cu(OH)_2$, 8 % H_3BO_3, 10 % polymer betain), a Cu-azole (Tanalith E 3492, Arch Timber Protection nv, Belgium; 20.5 % $CuCO_3$, 4.5 % H_3BO_3, 0.23 % tebuconazole, 0.23 % propiconazole) and a Cu-Quat (Kemwood ACQ 1900, CSI Kemwood AB, Sweden; 38-44 % copper tetra-amine-dihydrogencarbonate, 4.8 % N-alkyldimethylbenzylammoniumchloride QAC). It was decided to impregnate the wood with the preservatives at about 10 kg of product retention per m³ of sapwood. This is close to the average retention of these products as prescribed for usage under class AB of the Nordic Wood Preservation Council (NTR No 73 2005).

Scots pine sapwood specimens (15 × 25 × 50 mm³, R × T × L) were placed in a vessel and a vacuum was induced for 20 minutes before adding the solution to the vessel. After reinstalling the vacuum for 5 minutes, the vacuum was released and the specimens stayed submerged for another two hours. Afterwards the specimens were allowed to a fixation drying at ambient conditions for 48 hours and subsequently at 60 °C until they reached a constant mass. The masses prior to and after treatment were determined and allowed to calculate the obtained retention (Eq. 1.2).

Modified wood

In this research modified wood can be divided into two groups, namely thermally modified wood and furfurylated wood. The thermally modified spruce (*Picea abies*) used in this research was sampled during the development of the hydrothermal Plato-process. Furfurylated wood according to two different scaling up processes was also included. In the first process, SYP (30 % WPG) and maple (20-25 % WPG) were treated according to a furfurylation process using a monomeric furfuryl alcohol treating solution. For the second furfurylation process, SYP was treated according to a process applying an oligomeric furfuryl alcohol based solution (20-30 % WPG). The main end-uses for both thermally

modified and furfurylated wood are garden furniture, fencing, cladding and joinery (Hakkou et al. 2006).

5.2.2 Leaching procedures

It was the purpose of this study to set up a methodology to evaluate both the fungal resistance of the wood (either treated or modified) as well as the ecotoxicity. Since the preservative treated wood was aimed at use class 3 (EN 335-1 2006) the European Standard EN 599-1 procedure was followed. The specimens were first leached according to the European Standard EN 84 (1996) and then subjected to fungal decay according to the European Standard EN 113 (1996). For testing equivalent natural durability assessment reference is made to CEN/TS 15083-1 (2006) which is similar but not using dose-response as a basis.

Wegen et al. (1998) stated that for the ecotoxicity estimation testing of the 24 hours leachate is suited as a worst case consideration. Concerning the wood in service they recommend using the 14 day EN 84-leachate of treated timber. It is however a basic problem to generate a leachate containing realistic concentrations of depleted components (Melcher and Wegens 1999). Therefore a second series of treated wood blocks was subjected to the milder OECD part 1-leaching procedure (CEN/TR 15119 2005), developed for usage in use class 3. In view of equal treatment of all specimens also two series of the modified wood blocks were subjected to leaching, each series according to one of both leaching methods.

The leaching procedure according to the European Standard EN 84 was used as a worst case scenario. The 12 replicates for each treatment were divided into two groups. The volume water to wood ratio used was 5, i.e. 562.5 ml water for each 6 specimens. The leaching procedure consisted of an initial impregnation with distilled water. The water was subsequently replaced 2 hours after the impregnation and at 24 hours and 48 hours, and another seven times in the

next 12 days at intervals of not less than one day and not more than three days. The first (24h) and last leachates were retained for further use in the ecotoxicity tests. This leaching procedure differs from the OECD part 2-leaching procedure (OECD 1984), which is developed for wood in use classes 4 or 5 (EN 350-2 1994): (1) the cross sections of the specimens are not sealed in EN 84, (2) the ratio wood surface to water is 40 m^2/m^3, whereas this is 50 in OECD part 2, and (3) the exposure time is only 14 days according to EN 84 and 30 days according to OECD part 2.

A more realistic and much 'milder' OECD part 1 leaching procedure was also performed. Using this method, both cross sections were sealed with 2 layers of a 2-component polyurethane finish. This time the ratio wood surface area/water volume was kept constant at 40, being 600 ml of water for 6 specimens. No impregnation of the specimens was performed, but immersions in water were used to simulate rain events. One rain day consisted of 3 separate rain events. This means that the specimens were in groups of six specimens submerged 3 times a day in 600 ml distilled water during 1 minute. Between the submersions the specimens were allowed to dry under ambient conditions. In the next 14 days every third day was a rain day. The leachates were collected after the first and fifth rain day and used for ecotoxicity testing. Both pH and total hardness were determined on all leachates. To lower the impact of pH on the ecotoxicity testing the pH values lower than 6.0 were adjusted with NaOH (0.5 mol/l) to a value between 6.0 and 7.0.

5.2.3 Ecotoxicity testing

The ecotoxicity of the leachates was evaluated with the freshwater crustacean *Daphnia magna* using the Daphtoxkit procedure (Daphtoxkit F^{TM} magna 2001), which is based on the OECD guideline 202 (1984). Five concentration series of the pooled duplicate leachates (1:2 dilution series) using four replicates and a control series were used for each treatment. Five neonates were transferred to each well and the micro-well test plates were subsequently incubated for 48

hours in the dark at 20 °C. After 24 hours and 48 hours of exposure, the inhibition of mobility of the daphnids was recorded. The toxicity data obtained as 50 % effect endpoint values (EC_{50}s) in % of dilution were calculated according to the Trimmed Spearman-Karber method (Hamilton et al. 1977; US EPA 2006). The EC_{50} values were subsequently transformed into toxic units (TUs) with the formula of Sprague and Ramsay (1965) as cited in Manusadžianas et al. (2003) (Eq. 5.1).

$$TU = \frac{1}{EC_{50}(\%)} \times 100 \quad (5.1)$$

Since each leaching procedure yielded two leachates (both after 1 and 14 days) a multi-stage evaluation of the four leachates was considered. First of all the leachates originating from the harshest leaching procedure, being the EN 84-leachates obtained after 1 day, were evaluated, since it was considered that these leachates had potentially the highest environmental impact. If no significant toxicity for *D. magna* was observed, the evaluation stopped here, since real life leaching, which is milder, should not cause any toxic effect. If, in contrast, a considerable ecotoxicity was detected then a second step was performed. In this step both the EN 84-leachates after 14 days and the OECD part 1-leachates of the first rain day were examined. When these latter leachates still exhibited a toxic response, then the leachates of the fifth rain day (OECD part 1) were also evaluated. An arbitrary ecotoxicity evaluation scale was used based on the 1:2 dilutions of the leachates. In that respect leachates with less than 2 TUs were considered not toxic, especially since all leachates of untreated wood belong to that class (see results). They are being used already for a long time in use class 3 conditions and considered socially acceptable. In line with this in this paper the consecutive classes are called hardly toxic (2-4 TUs), slightly toxic (4-8 TUs), toxic (8-16 TUs) and quite toxic (> 16 TUs).

5.2.4 Decay resistance

The evaluation of the protective effectiveness against basidiomycetes of the Scots pine sapwood specimens treated with wood preservatives was done based on the European Standard EN 113 (1996). However no concentration range was considered, but merely one treating level was assessed. In contrast, modified wood cannot be evaluated using the wood preservatives approach, but could be evaluated based on the natural durability approach (CEN/TS 15083-1 2006). Although modified wood is not a new wood species, the characteristics of the original wood species are changed in such a radical way that they could be considered as a new wood species/product (Van Acker 2003).

Both the EN 113 and the CEN/TS 15083-1 tests are very similar and hence the test set-up used allows several approaches. After the leaching procedures, the wood blocks were given the time to dry at ambient conditions and they were subsequently γ-sterilised. Kolle flasks with a malt-agar culture medium were inoculated with *Coniophora puteana* or *Postia placenta* for softwood (Scots pine sapwood and spruce) and with *Coniophora puteana* or *Trametes versicolor* for hardwood (maple). In each EN 113 test flask, one untreated control wood block was put beside one preservative treated wood block. However, in each CEN/TS 15083-1 test flask, two modified wood blocks were put next to each other. For both test set-ups untreated control specimens were used to test the virulence of the fungi. To take factors that have an influence on the mass other than fungal attack into account, additional preservative treated/modified wood blocks were aseptically put into un-inoculated culture vessels to determine a correction factor C. After sixteen weeks exposure, adhering mycelium was taken away and the specimens were weighed after oven drying at 103 °C, which allowed calculating the mass loss (Eq. 5.2).

$$ML\ (\%) = \left[\frac{m_{untreated} - m_{dry}}{m_{untreated}} \times 100\right] - C \qquad (5.2)$$

5.3 Results

5.3.1 Ecotoxicity evaluation

The ecotoxicity results obtained for the various treatments are summarized in Table 5.2. As the table indicates no considerable toxicity (<2 TUs) was observed for untreated wood, and this is valid for all wood species and leaching methods evaluated. As can be expected a pronounced ecotoxicity was determined for wood treated with Cu-based preservatives. No difference in ecotoxicity could be observed for the Cu-based preservatives based on the leachates after 24 hours EN 84-leaching, since they all show TU values over 16. After 14 days leaching the leachates of Scots pine sapwood treated with CCA (4.9 TUs) or Cu-Quat (4.5 TUs) are classified as slightly toxic, whereas leachates of treatments with Cu-azole (2.6 TUs) are rated hardly toxic and leachates of treatments with Cu-amine (<2 TUs) are considered not toxic. The ecotoxicity of leachates obtained according to the OECD part 1-procedure for nearly all treatments is lower than those after 14 days EN 84-leaching. Treatments of Scots pine with CCA or a Cu-azole are rated as being not toxic (<2 TUs) while treatments with a Cu-amine (2.6 TUs) or a Cu-Quat (3.7 TUs) are still considered hardly toxic. Therefore these last two leachates after 14 days OECD part 1-leaching were analysed. This led to the conclusion that the leachates were no longer toxic after 14 days OECD part 1-leaching (<2 TUs).

Table 5.2 also indicates that both the modification process and the wood species influence the ecotoxicity response to *D. magna* of modified wood. Leachates of thermally treated spruce were hardly toxic (3.6 TUs) after 24 hours EN 84-leaching and the ecotoxicity even diminished after 14 days or when leached according to the OECD part 1-leaching (1-day). These last two leachates were classified as not toxic (<2 TUs). Wood furfurylated with a monomeric FA solution displayed certain ecotoxicity and this toxicity seems to depend both on the wood species as well as on the leaching procedure. SYP leachates seem to have an inherent lower toxicity than leachates of maple, although they have a slightly higher WPG (30 % WPG for SYP compared to 20-

25 % WPG for maple). The EN 84-leachates of the furfurylated SYP were classified as slightly toxic (5.8 TUs), whereas those of furfurylated maple were quite toxic (>16 TUs). A striking point of agreement between the two wood species furfurylated with the monomeric solution, is the fact that the toxicity does not seem to diminish over time. The ecotoxicity towards *D. magna* of leachates of oligomeric furfurylated SYP has astonishing low values. The ecotoxicity was, regardless the leaching procedure and harvesting time, always considered not toxic (<2 TUs).

Table 5.2: Product retention values and ecotoxicity (expressed as toxic units at 48 h) to *Daphnia magna* of the leachates of the treated wood

Wood species/Treatment	Toxic units for different leaching procedures			
	EN 84		OECD part 1	
	1 day	14 days	1 day	14 days
Untreated softwoods				
Scots pine sapwood	<2	<2	<2	-
Scots pine heartwood	<2	-	-	-
Douglas fir	<2	-	-	-
Untreated temperate hardwoods				
Beech	<2	-	-	-
Oak	<2	-	-	-
Black locust	<2	-	-	-
Untreated tropical hardwoods				
Abiurana	<2	-	-	-
Azobé	<2	<2	-	-
Bangkirai	<2	-	-	-
Merbau	<2	<2	-	-
Padauk	<2	-	-	-
Piquia	<2	-	-	-
Wood[1] treated with preservatives				
CCA at 10.4 kg/m³	>16	4.9	<2	-
Cu-azole at 11.3 kg/m³	>16	2.6	<2	-
Cu-amine at 10.9 kg/m³	>16	<2	2.6	<2
Cu-Quat at 10.8 kg/m³	>16	4.5	3.7	<2
Modified wood				
Furfurylated SYP[2] (process 1)	5.8	7.5	<2	-
Furfurylated maple[3] (process 1)	>16	>16	<2	-
Furfurylated SYP[2] (process 2)	<2	<2	<2	-
Thermally modified Spruce[4]	3.6	<2	<2	-

- = EC_{50} not determined; [1]: Scots pine sapwood, *Pinus sylvestris* L.; [2]: *Pinus* spp.; [3]: *Acer pseudoplatanus* L.; [4]: *Picea abies* (L.) Karst

5.3.2 Fungal resistance

Since the natural durability of the untreated wood species is already known (Table 5.1), they were not determined again. Figure 5.1 gives an overview of the mass losses obtained for the preservative treated and modified wood after exposure to various fungi during 16 weeks. The figure shows that both the CCA and Cu-azole treated Scots pine specimens were fully protected against fungal attack by both *C. puteana* and *P. placenta*. The Cu-amine treated wood in contrast was treated at a retention level below the toxic value and could not be differentiated from untreated Scots pine sapwood. This indicates that the wood was not sufficiently protected at a retention level of circa 10 kg/m³. The Cu-Quat treated specimens show a sufficient protection against attack by *C. puteana* since the mass loss is below the 3 % limit; however the mass losses caused by *P. placenta* were considerably higher.

For the thermally modified spruce the mass loss caused by *P. placenta* did not differ from that of untreated spruce, whereas the mass loss of the wood induced by *C. puteana* was below the 3 % threshold (Figure 5.1). Both furfurylation processes could reduce the decay of SYP by *C. puteana* and *P. placenta*, although none of them could be identified as full preservative effective. The furfurylated maple is protected effectively both against attack by the brown rotter *C. puteana* and the white rotter *T. versicolor*. When considering modified wood as a new wood species, the natural durability can be determined based on the mass losses obtained after 16 weeks exposure to the fungi (CEN/TS 15083-1 2006). The durability class should be determined using the highest mass loss and so the thermally modified spruce ends up in durability class 5, despite the good protection against *C. puteana*. The monomeric furfurylation of SYP induced an improvement in durability with 2 classes, whereas the oligomeric furfurylation process can enhance the durability with only 1 class. Due to the furfurylation maple is rated in durability class 1, whereas untreated maple is rated 5. This again shows that not only the ecotoxicity, but also the fungal resistance is influenced both by the wood species as well as by the modification process parameters.

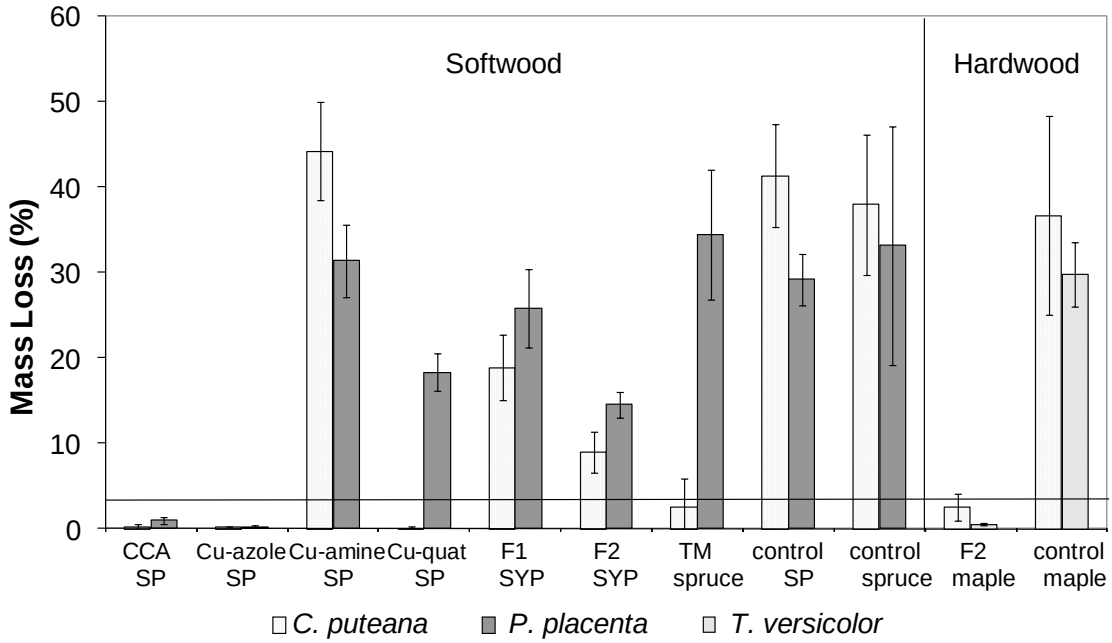

Figure 5.1: Mass loss of Scots pine sapwood (SP) specimens impregnated with four different Cu-based wood preservatives, furfurylated (F) southern yellow pine (SYP) and maple, thermally modified (TM) spruce and control specimens. The horizontal line is situated at 3 % mass loss

5.4 Discussion

5.4.1 Ecotoxicity evaluation

Table 5.3 gives an overview of ecotoxicity values for leachates from different wood species and treatments as presented in literature. The table confirms for nearly all evaluated untreated wood species that their leachates are not toxic (<2 TUs) towards *D. magna* (Van Eetvelde et al. 1997; Van Eetvelde et al. 1998). This is also valid for the tropical wood species, which have an inherent toxicity due to the presence of extractives. This means that, despite the pronounced colour of the leachates due to the presence of extractives, they are not rated toxic to *D. magna* under the circumstances as described in this paper. The data show the importance of the leaching regime since azobé, padauk and merbau give different toxicity values depending on the leaching procedure used. The highest values are recorded for leachates obtained according to the ENV 1250.2-leaching procedure (ENV 1250-2 1994; Van Eetvelde et al. 1998),

followed by those acquired according to the OECD part 2 leaching procedure (Van Eetvelde et al. 1997). The values obtained with the leaching regimes in this research are even lower (Table 5.2). It is known that the ENV 1250.2 procedure is harsh, mainly due to stirring of the water during leaching. The OECD part 2 procedure is designed to test wood exposed under use classes 4 and 5, which are the highest possible use classes (EN 335-1 2006). In fact it is more or less a modification of the biological efficacy testing protocol EN 84 which is developed to test wood used under use class 3 conditions (Willeitner and Peek 1998). This EN 84-leaching is still considered to be severe due to the water impregnation stage (Hingston et al. 2001). The OECD part 1-leaching procedure wants to assess leachates in use class 3. Despite the important influence of the leaching procedure it still stays surprising that merbau gives rise to such a high variation in ecotoxicity.

The thermally modified spruce used in this study showed low toxicity of the leachates towards the crustacean *D. magna*. Although even lower toxicities, obtained with the ENV 1250.2-leaching method, are reported by Van Eetvelde et al. (1998) for Plato treated Scots pine and beech, the TUs found in this research for EN 84-leachates after 1 day of thermally modified spruce are still classified as hardly toxic (3.6 TUs). This research shows that whatever compounds are formed during the heat treatment of spruce as used in this research, the leachable part is only slightly to not toxic to the crustacean *D. magna*.

The ecotoxicity of furfurylated wood was earlier reported by Lande et al. (2004a). They reported no toxicity (<2 TUs) towards *D. magna* for VisorWood leachates. This VisorWood is Scots pine furfurylated according to the same process as Kebony, but with a different treating solution (Hakkou et al. 2006). Lande et al. (2004a) put forward two reasons for the low leachate toxicity of VisorWood. The first reason could be that the furfurylated pine wood consisted mainly of sapwood with low extractive content. It is believed that the differences in natural extractive quantities are the reason for the differences among the pine

samples tested and not the furfurylation process. The second reason could be the reaction between FA and the extractives. Reaction may immobilize some of the extractives, thereby reducing their leachability. These reasons seem only partly valid for the furfurylated wood in this research. This research proved that the extractives of both untreated Scots pine sapwood and heartwood are not toxic to *D. magna*. This means that differences in natural extractive quantities of Scots pine, being present between sapwood and heartwood, cannot lead to a toxic response in one case and a non-toxic response in another case of the leachates towards *D. magna*, although they might be responsible for small differences in ecotoxicity among samples.

SYP furfurylated according to the first process using monomers has a slightly toxic leachate (5.8 TUs) whereas the one treated according to the second process using oligomers was not toxic (<2 TUs). The difference in ecotoxicity between the two furfurylation processes is however very significant. It is likely that the treating solution and process parameters (including the curing and drying step) during furfurylation play an important role in this. They may therefore also influence the possible reaction between FA and extractives. Also the wood species as such seems important. Monomeric furfurylated maple (20-25 % WPG) gives higher leachate toxicity than monomeric furfurylated SYP (30 % WPG). The authors therefore do believe that the differences in ecotoxicity are caused by a combination of factors: wood species, treating solution, WPG and furfurylation process used. Because of the complexity of parameters having their influence on the leachate toxicity and the limited knowledge on the influence of each of them on the global ecotoxicity, it remains difficult to make an overall statement about the ecotoxicity of leachates of furfurylated wood against *D. magna*. The overall conclusion on furfurylated wood is that impact on ecotoxicity of leachates can be steered by means of optimised treatment parameters.

Van Eetvelde et al. (1998) have reported toxicities of Scots pine treated with different Cu-based formulations. Regardless the type of Cu-based formulation,

all EN 1250.2-leachates had a toxicity of over 32 (Table 5.3). This is in correspondence with the high toxicities found in this research with the EN 84-leaching method. However no exact TUs were determined in the range over 16. Table 5.2 also shows that there is a rapid decline in toxicity after 14 days. This indicates the decrease in leachable components over time. The low TUs found after 24 hours OECD part 1-leaching prove positive assessment for long term usage of preservative treated wood.

The multi-stage approach has an added value over evaluating the ecotoxicity of a single leachate. For determining the protective effectiveness of wood preservatives, the EN 84-leaching can be used as ageing method. If only the first leachate after 1 day was evaluated, no distinction between the Cu-based treatments would have been possible. The distinction in ecotoxicity of their leachates is possible due to the subsequent evaluation of the EN 84-leachates after 14 days. Comparing the TUs of both harvesting periods with each other learns that the ecotoxicity towards *D. magna* of leachates of preservative treated wood diminishes fast over time, while this is not the case for modified wood. Since thermally modified spruce and oligomeric furfurylated SYP already had low TUs after 1 day, this is not surprising. But as stipulated before, this constant toxicity over both harvesting periods is marked for monomeric furfurylated SYP and maple. Considering the OECD part 1-leachates no ecotoxicity was detected.

As comprehensive conclusion of this multi-stage evaluation it can be said that preservative treated wood has an impact on the environment when exposed under heavy duty conditions, but this ecotoxicity diminishes fast with time. When in contrast the preserved wood is used in less severe circumstances, the leachates seem to have limited impact on the environment. For modified wood, the conclusion depends on the modification process used. Leachates of thermally modified spruce and oligomeric furfurylated SYP are considered only slightly to not toxic, regardless the exposure conditions. When SYP or maple is furfurylated with a monomeric solution, the ecotoxicity clearly depends on the

exposure conditions; the harsher they are, the more the leachates pose a threat to the environment. Ongoing research showed that not the treating solution as such, but more specifically the treatment process parameters influence the leachability of compounds.

Table 5.3: Literature values of the toxicity of leachates of different wood products (expressed as toxic units) to *Daphnia magna*

Wood species	Exposure time		
	24h[1]	24h[2]	48h[1]
Untreated wood			
Scots pine sapwood	-	<2	<2
Oak	-	-	<2
Black locust	-	-	<2
Azobé	3.3	<2	4.4
Bangkirai	<2	<2	<2
Merbau	> 32	16.7	>32
Padauk	-	-	2.5
Wood treated with preservatives			
CCA-C Scots pine	-	-	>32
CCB Scots pine	-	-	>32
Cu-organic at 10 kg/m³	-	-	>32
Cu-organic at 8 kg/m³	-	-	>32
Modified wood			
Scots pine Plato	-	-	2.3
Beech Plato	-	-	<2
Scots pine Visor Wood (furfurylated)	-	-	1.5[3]
Scots pine (acetylated)	-	-	3.7

[1]: Leached according to ENV 1250.2 (ENV 1250-2 1994; Van Eetvelde et al. 1998); [2]: Leached according to OECD 202 part 2 (OECD 1984; Van Eetvelde et al. 1997); [3]: Leached according to EN 84(EN 84 1996; Lande et al. 2004a)

In view of the most realistic leaching procedure and ecotoxicity test for wood applied in use class 3 conditions, the OECD part 1-leachates after 1 day exposure and consecutive evaluation of immobility of *D. magna* after 48 hours seem the most suited. Evaluated in this way, the untreated wood species are all classified as non toxic. For the preservative treated wood, only those impregnated with about 10 kg/m³ Cu-amine or Cu-Quat showed low toxic values and none of the modified wood specimens gave toxic leachates. Nevertheless it must be stressed that the ecotoxicity of the leachates was evaluated with only the crustacean *D. magna*. For a more comprehensive ecotoxicity profile,

organisms of different trophic levels should be included. Whereas also (sub)chronic/long-term ecotoxicity are important, they are out of the scope of this paper and therefore not examined.

5.4.2 Fungal resistance

Increased durability of thermally modified wood has been reported by several authors (Boonstra et al. 1998; Kamdem et al. 2002). Research has indicated that the change in wood properties depends upon the species treated and the exact conditions employed in the process. Tjeerdsma et al. (1998) stated that heat treatment according to the Plato-process revealed the highest improvement for its resistance against brown rot fungi and more specifically against *C. puteana*. This is confirmed in this research where the resistance of the thermally modified spruce against the brown rot *C. puteana* was increased a lot (mass loss below 3 %), but the efficacy against *P. placenta* did not differ significantly from the one of untreated spruce. Several authors state that the exact conditions of heat treatment have a significant effect on improved properties. This means that by changing the process parameters emphasis can be put on strength, dimensional stability or durability (Tjeerdsma et al. 1998).

Although Kebony 30 is classed as durable and Kebony 100 as highly durable (Hill 2006), not many publications provide detailed information of biodegradation of furfurylated wood. Lande et al. (2004b) reported that furfurylation of wood gave high protection against biodegradation (fungi, marine borers and termites) at moderate to high levels of modification. They found reduced mass losses after 16 weeks for VisorWood treated Scots pine specimens treated at 20-75 % WPG, whereas full protection (ML <3 %) against *P. placenta* was achieved at a WPG level of 120 %. All mass losses were lower than 10 % and thus all furfurylated material can be allocated to durability classes 1 and 2 (CEN/TS 15083-1 2006). In this research only furfurylated maple (20-25 % WPG) achieved durability class 1, to which also padauk, azobé and to a lesser extent also abiurana and black locust belong. This is a considerable improvement in

durability compared to untreated maple which is rated not durable just like untreated beech or Scots pine sapwood (durability class 5). For SYP moderate improvements from durability class 5 to 4 or 3 were recorded, depending on the furfurylation process used. This is quite good, since the furfurylated wood is mostly used in use class 3 conditions. Douglas fir, oak, piquia and Scots pine heartwood are also used under this biological use class without additional treatment.

Although CCA serves already a long time as wood preservative and has shown its efficacy in practice (Hingston et al. 2001; Mazela et al. 2005), not many data are provided on the toxic values for basidiomycetes attack. Cockroft (1974) collected the data available in 1974 and reported that the toxicity value for CCA treated Scots pine amounted 2.3 ± 1.4 kg/m³ and 2.7 ± 0 kg/m³ against *C. puteana* and *P. placenta*, respectively. In this research it was not the purpose to determine this toxic value, but to evaluate the performance of Scots pine impregnated as currently in use. The sapwood retention of 10.4 kg/m³ CCA, which is higher than the approved one by the Nordic Wood Preservation Council (NTR No 73 2005), was anyhow able to protect the wood completely. It can therefore be expected that lower loadings would also suffice to protect the wood. Humar et al. (2004) were able to show that after 10 years outdoor exposure CCA treated Scots pine (6.9 kg/m³ of CCA) was still able to protect the wood sufficiently based on brown rot decay resistance in an EN 113 test. This was valid for both copper sensitive strains and a copper tolerant strain. In contrast Tanalith E impregnated specimens (1.8-1.9 kg/m³ of Cu) could only protect the wood sufficiently against attack by *Gloeophyllum trabeum* and not against *P. placenta*. In this research the loadings of Cu-azole were lower, but slightly higher than the ones approved (NTR No 73 2005) and full protection was achieved against both *P. placenta* and *C. puteana*. Of course it is not possible to fully compare the 10 year natural weathering with artificial weathering/leaching according to EN 84. Both the Cu-amine and the Cu-Quat were applied at a lower loading than the ones approved (NTR No 73 2005), so it

could be expected that higher protection can be achieved with higher concentrations.

To evaluate the performance of treated wood under use class 3 conditions against basidiomycetes, both the natural durability approach and the preservative approach can be used. This research has shown that equal performance can be achieved using the biocidal strategy applying Cu-based solutions or when modifying the wood.

To determine the durability, evaluation according to CEN/TS 15083-1 seems the best option. The determined durability should at least be equal to 3 to be suited to use the wood in outdoor conditions out of ground contact. Table 5.1 shows that all untreated wood species, except Scots pine sapwood and beech, are classified in durability class 3 or higher. This classification was made based on durability according to EN 350-2 (for in ground contact) and practice. The preservative treated wood considered in this paper was not tested using a dose-response as in EN 113, but as induced durability evaluated similar to natural durability (Figure 5.1). The Cu-amine and Cu-Quat treated wood were not fully durable, nevertheless was the Cu-Quat treated wood at the limit for durability class 3. Concerning modified wood furfurylated maple was classified as very durable. Monomeric furfurylated SYP (30 % WPG) reached durability class 3 and was therefore in the light of this research, sufficiently treated. When SYP is furfurylated using the oligomeric solution (20-30 % WPG) a durability close to the one of class 3 is obtained. The wood might therefore require a slightly higher treatment level. Since the tested thermally modified spruce is not durable against *P. placenta* but very durable against *C. puteana* there seems to be options for improvement of the treatment conditions. Performance in practice can however differ significantly from the lab test results since the protection mechanism induced is moisture control driven and lab tests enforce higher moisture content. Similar data could be observed for Scots pine heartwood (Van Acker et al. 1999). Therefore field tests are needed to get a full picture of the performance of preservative treated and modified wood in practice.

5.4.3 Combining ecotoxicity and efficacy

The monomeric furfurylated maple in this research could resist fungal attack very well and is classified as very durable. In contrast its leachates after 1 day and 14 days EN 84-leaching are rated as quite toxic (>16 TUs). The same tendency, although less marked, is observed for the monomeric furfurylated SYP using the same process. The improvement in protective efficacy against basidiomycetes is limited to durability class 3, but the corresponding ecotoxicity of the EN 84-leachates is also limited to slightly toxic (4-8 TUs). For the oligomeric furfurylated SYP the efficacy against basidiomycetes is only slightly improved to durability class 4, but the corresponding ecotoxicity is very low and in the same range as the one of untreated wood (<2 TUs). The thermally modified spruce leads to some confusing results in that way that the efficacy against *P. placenta* is not improved at all compared to untreated spruce, whereas the durability against *C. puteana* is very high. The ecotoxicity of the leachates against *D. magna* is hardly toxic (2-4 TUs) to not toxic (<2 TUs), depending on the leaching procedure used.

For the preservative treated Scots pine, irrespective the type of Cu-based formula used, the EN 84-leachates of the treated wood after 1 day are quite toxic (>16 TUs). But, as stipulated before, this toxicity diminishes fast over time (14 days EN 84-leaching). Although no important differences in ecotoxicity towards *D. magna* are observed, major differences in efficacy can be observed. Both CCA and Cu-azole treatments are very effective in protecting the wood against fungal attack at the retention used. For the Cu-Quat treatment a discrepancy in protective effectiveness between different fungi is found. Since the Cu-amine treatment of Scots pine sapwood resulted in a lower concentration than approved by the Nordic Wood Preservation Council, higher retention rates are desirable to achieve good protection of the wood against fungal attack.

5.5 Conclusion

Most ecotoxicity TUs determined in this research are in line with what has been reported in literature. Those values that differ from literature could be attributed to differences in leaching procedures. Again it is shown that the type of leaching procedure is crucial in the assessment and should therefore always be mentioned when reporting leaching or ecotoxicity values (Waldron et al. 2003). Combining the results of the ecotoxicity study and the wood protection efficacy test of each product reveals that certain products can guarantee a good protection, but have a high ecotoxicity value and vice versa. The methodology proposed in this research could help to develop a product/process aiming for treatment of wood to be used under use class 3 conditions, since it may help to find a good balance between the efficacy against decay by basidiomycetes and the ecotoxicity of the leachates of the treated wood.

This research used a range of treated wood materials at a chosen treatment level or even using process conditions still being optimised. The indications of commercial products are not intended to evaluate them in general but the specific test material was mainly to stimulate extra discussion on the importance to use material fit for purpose for use class 3 applications. High retention values or more harsh treatment conditions might induce higher ecotoxicity of the leachates. Some close to optimal conditions resulted in results which do not necessarily correspond to practice. This seems to be the case for the furfurylated maple and SYP used in this research, which were not yet treated under optimal conditions. Scots pine sapwood impregnated with Cu-Quat and even more with Cu-amine would require a somewhat higher retention level to perform adequately. The retention levels used here reveal however the difficulty with increased ecotoxicity. Tropical wood species were included in this work as they are considered functional and fit for purpose for use class 3 applications and might be considered for benchmarking both for durability and ecotoxicity assessment. The methodology as applied in this paper proves to be suited to evaluate both parameters adequately and may therefore be used during the development phase of a new product as well as at the final certification of it.

Acknowledgements

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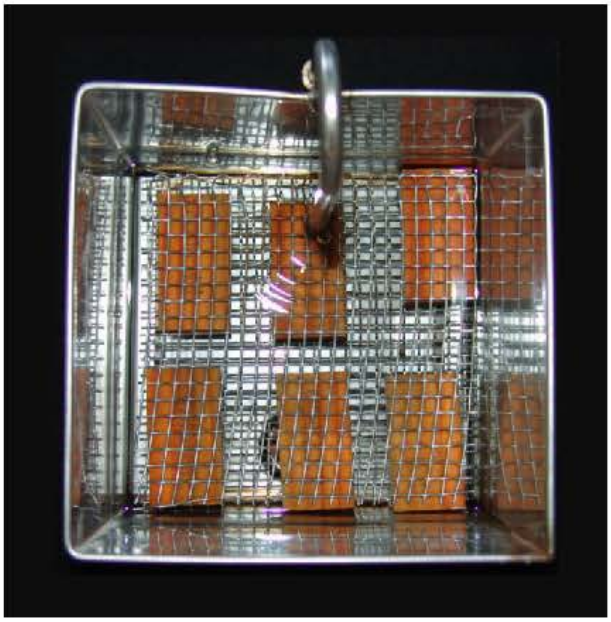

6 POTENTIAL CONTRIBUTION OF ORGANOSILICON COMPOUNDS TO REDUCED LEACHING OF BIOCIDES IN WOOD PROTECTION[1]

Abstract

Leaching of biocide treated wood leads to reduced effectiveness and potential threat to the environment. Therefore the effectiveness of organosilicons as protective systems of biocides was evaluated. Scots pine sapwood specimens were impregnated with solely organosilicons and biocides as well as with combinations of both. The biocides 3-iodo-2-propynylbutylcarbamate, propiconazole and 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride confirmed their effectiveness regardless the addition of an organosilicon. Low leachate toxicities to the crustacean *Daphnia magna* were found for the organosilicons, whereas significant leachate toxicities were measured for the biocides. Combining both did not considerably diminish the leachate toxicities. It must therefore be concluded that under the circumstances as described in this article, organosilicons do not interfere with the efficacy of the biocides, but they do not contribute to a reduced leaching of the biocides either.

[1] Published as:
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6.1 Introduction

Biocides are often applied by impregnation to protect less durable wood from degrading organisms. Practice has revealed that a lot of these biocides are subjected to leaching, potentially harming other living organisms. Furthermore, once the retention of the biocides in the wood falls below a certain threshold, the retained biocides are no longer able to protect the wood adequately. It has been suggested that water repellents like oils, waxes and silicones, can be combined with biocides for wood in use class 3 conditions being outdoor usage out of ground contact (Donath et al. 2006a, 2006b). The primary purpose of these products is to interfere in the wood-moisture relation to protect the wood, but they are also supposed to prevent leaching of biocides during service life (Zahora 2000; Taylor and Cooper 2003; Mai and Militz 2004b; Donath et al. 2006a, 2006b). Their suitability, mode of action and location inside wood once applied has been investigated (Sèbe and Brook 2001; Ritschkoff et al. 2003; De Vetter and van Acker 2005; De Vetter et al. 2006) . Although some positive results, also conflicting data are reported about the effect of water repellents, e.g. differential leaching of arsenic, chromium and copper (Cui and Walcheski 2000; Lebow et al. 2004).

Focus in this study was on three different biocides used in wood preservative formulations. The carbamate 3-iodo-2-propynylbutylcarbamate (IPBC) was proved to be effective in protecting wood against blue stain, moulds and degrading fungi. Drawbacks are its known toxicity towards fish and daphnids (Cook et al. 2002). Testing quaternary ammonium compounds showed their effectiveness as wood protecting agents, but they may leach out and pose a threat to both mammals and humans (Donath et al. 2006b). The triazole fungistatic compound propiconazole prevents or blocks fungal growth by binding to the enzyme sterol 1,4α-demethylase, thereby preventing synthesis of ergosterol, an essential part of fungal cell walls (Zarn et al. 2003). It has a good penetration and distribution in wood and a good toxicological profile and is being used to protect crops and wood (Valcke 1989; Kurti et al. 2005).

The purpose of this research was to find out whether organosilicon compounds are able to lower biocide leaching without compromising the biocide-efficacy in protecting wood from degradation. If they do so, it is assumed that the leachates contain less biocide compared to wood treated with solely biocides and have therefore a lower impact on the environment. It is clear that both efficacy and ecotoxicity are important in this evaluation. That is why the method described by De Vetter et al. (2008) was used for this investigation.

6.2 Materials and methods

6.2.1 Treatments of specimens

Scots pine sapwood specimens (25 × 15 × 50 mm³, R × T × L) were vacuum impregnated with the silicon containing organic compounds W1, W2, W3, W4, S1 and S2, which were applied at 5 % active ingredient concentration. Besides the organosilicons the three biocides B1, B2 and B3 were used in this research. Biocide B1 (IPBC) was used at 0.3 % active ingredient, just like biocide 3, where 0.3 % of the first component IPBC corresponds to 0.6 % of the second component propiconazole. Biocide 2 (Si-Quat) was applied at 2 % in water, while it was diluted to 1 % when applied in isopropylalcohol. Alongside treatments with organosilicons and biocides separately, also combinations of both were made. Therefore organosilicons W2 and S2 were combined with each of the biocides and this at the same concentrations as applied alone. Only exception was the combination of 10 % active ingredient S2 instead of 5 % when combined with 1 % B2. Twelve replicates were used per treatment. More explanation about the organosilicons and the biocides themselves and the exact treatment conditions is given previously (1.3).

6.2.2 Efficacy and ecotoxicity of silicone-treated wood

The efficacy and ecotoxicity of silicone-treated wood was evaluated according to the methodology described by De Vetter et al. (2008). These results were then used as a basis to determine the biocides-fixation capacity of organosilicons. Scots pine sapwood specimens were, once treated, subjected to leaching and afterwards exposed to fungal decay. This methodology comprises a tiered approach of the ecotoxicity of the leachates towards the crustacean *Daphnia magna*. The leaching procedure according to the European Standard EN 84 (1996) was used as a worst case scenario. The method according to the OECD part 1-leaching (CEN/TR 15119 2005) was included as a milder, more realistic procedure. The first procedure comprises an impregnation of the wood specimens, followed by refreshments of the leaching water, whereas the second procedure simulates rain events by immersions in water. For both procedures the leachates at 24 hours and at 14 days were retained for further investigations.

The freshwater crustacean *Daphnia magna* was used to evaluate the ecotoxicity of the obtained leachates. The Daphtoxkit procedure (Daphtoxkit F^{TM} magna 2001) is based on the OECD guideline 202 (1984). Neonates were exposed to a 1:2 dilution series of the pooled leachates and incubated in the dark at 20 °C. The inhibition of mobility of the daphnids was determined after 48 hours exposure and the Trimmed Spearman-Karber method (Hamilton et al. 1977; US EPA 2006) was used to calculate the toxicity data being 50 % effect endpoint values (EC_{50}s) in % of dilution. These EC_{50} values were subsequently transformed into toxic units (TUs) with the formula of Sprague and Ramsay (1965) as cited in Manusadžianas et al. (2003) (Eq. 6.1).

$$TU = \frac{1}{EC_{50}(\%)} \times 100 \qquad (6.1)$$

First all 24 hour EN 84-leachates were evaluated. For those treatments showing significant toxicity the 14 day EN 84-leachate and the 24 hour OECD part 1-

leachate were assessed. When still significant ecotoxicity was observed the 14 day OECD part 1-leachate could also be evaluated. The limit for non-toxicity of 2 TUs as defined by De Vetter et al. (2008) was taken as the threshold value for significant toxicity.

The efficacy against wood rot of the leached Scots pine sapwood specimens was tested by exposure to the brown rot fungus *Coniophora puteana* using a malt-agar block method for 16 weeks (EN 113 1996). After exposure the specimens (six replicates) were removed from the Kolle flasks, adhering mycelium was taken away and the blocks were dried at 103 °C and weighed (m_{dry}) to determine the percentage mass loss (ML) of the wood substance, taking into account a correction value C linked to non-fungal mass loss (Eq. 6.2).

$$ML\ (\%) = \left[\frac{m_{untreated} - m_{dry}}{m_{untreated}} \times 100\right] - C \qquad (6.2)$$

6.3 Results

6.3.1 Efficacy and ecotoxicity of silicone treated wood

First of all the efficacy and ecotoxicity of organosilicon treated wood was determined. Figure 6.1 gives the WPGs of the silicones of the treated wood. Figure 6.2 illustrates that when the mass losses due to fungal attack are evaluated according to the European Standard EN 599 (1996), no single treatment can protect Scots pine sapwood effectively against attack by the brown rotter *C. puteana* since all mass losses are higher than the critical value of 3 %. However, when the mass losses are used to determine the durability class according to CEN/TS 15083-1 (2006) the results can be interpreted differently. Figure 6.2 shows that the solvent-based MTM/n-OTES (S2) and the 40 Wt % water-based DMS/n-OTES (W2) improve the durability of Scots pine sapwood from class 5 to class 4. The water-based 100 Wt % PDMS/TES (W4)

applied at 5 % ai concentration can improve the decay resistance of Scots pine against *C. puteana* with even two durability classes. These results indicate that both water- and solvent-based organosilicons applied at low concentrations are able to induce an improvement in durability of Scots pine up to durability class 3. However they do not reach full protection like wood preservatives (De Vetter et al. 2008).

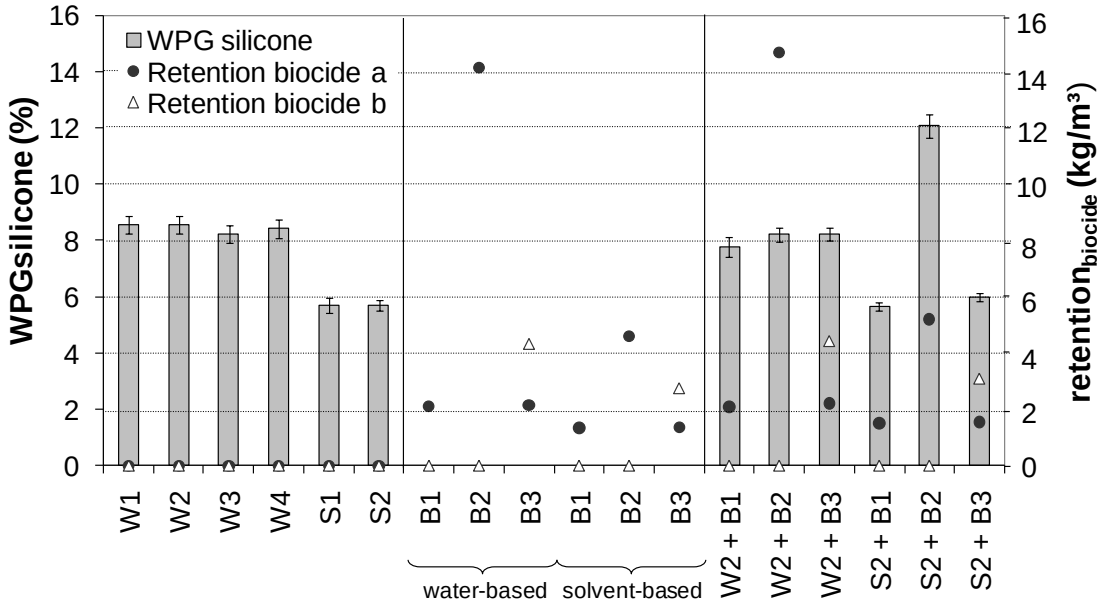

Figure 6.1: WPGs of organosilicons and retention values of biocides when vacuum impregnated into Scots pine sapwood EN 113-blocks. The average WPGs and their standard deviations are presented

The ecotoxicity values of the EN 84-leachates after 1 day are very low and all below 2 TUs (Figure 6.3). Since these leachates are obtained with the harshest method it can be concluded that organosilicon treated wood will most probably not pose any threat to the environment when used outdoors under out of ground contact conditions (EN 335-1 2006). The assessment of the ecotoxicity against *D. magna* of the other, milder leachates was therefore not carried out.

6.3.2 Efficacy and ecotoxicity of biocide treated wood

The biocide retentions of the different impregnations are presented in Figure 6.1. Figure 6.2 shows that all mass losses of Scots pine sapwood treated with

biocides and exposed to *C. puteana* are below the critical value of 3 %, indicating they fulfil the requirements of an effective wood preservative treatment (EN 599 1996).

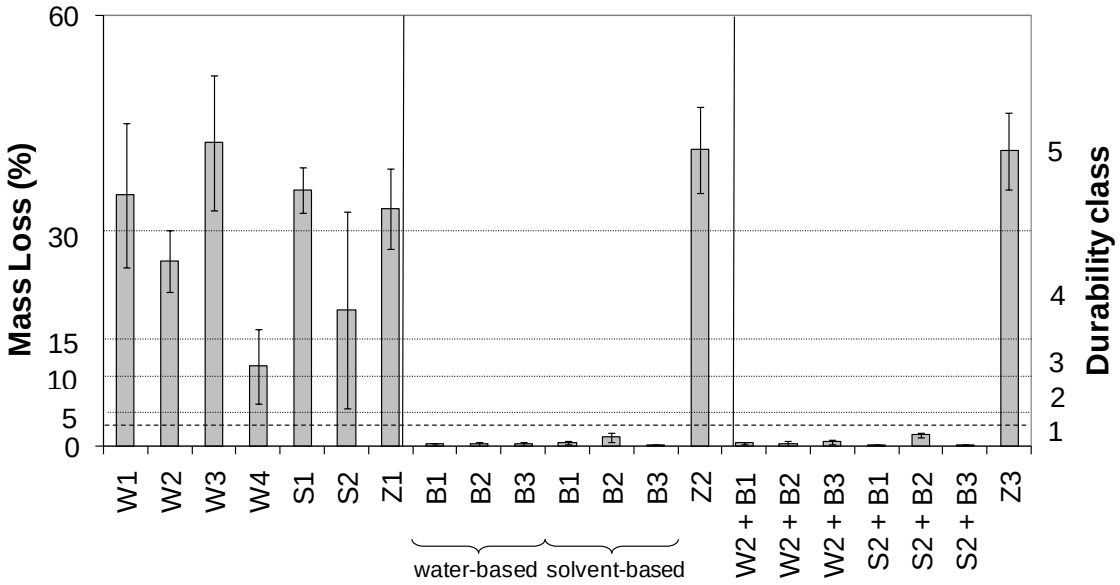

Figure 6.2: Mass loss and durability class of EN 84-aged Scots pine sapwood EN 113 specimens treated with organosilicons (W1 to S2), biocides (B1, B2 or B3) or both after 16 weeks exposure to *C. puteana*. The averages and their standard deviations are presented. The dashed line represents the critical value of 3 % mass loss for full preservative effectiveness

The toxic units of the leachates differ from each other (Figure 6.3). Wood treated with IPBC (B1) yields 1 day EN 84-leachates having extremely high TUs, respectively 84 and 74 TUs when applied in a water-based or solvent-based solution. These leachates with extremely high TUs are followed by the leachates of wood treated with a combination of IPBC and propiconazole (B3), yielding approximately 30 TUs. The least toxic leachates are those originating from wood treated with either 1 or 2 % ai Si-Quat (B2). The lowest (solvent-based) concentration gives rise to 6 TUs, whereas the highest (water-based) concentration results in 11 TUs. The difference in toxicity of the leachates by a factor 2 (11/6 TUs) is corresponding to the proportion of the concentrations in Si-Quat (2/1 % ai) between the water-based and solvent-based solutions. The observed leaching of the Si-Quat therefore appears to be concentration

dependent. Since the 1 day EN 84-leachates are resulting in TU values higher than the limit value of 2, the EN 84-leachates after 14 days and the OECD part 1-leachates after 1 day were also examined. Except for the water-based treatments containing IPBC or IPBC plus propiconazole having 6 and 5 TUs respectively, the TUs of these leachates are below the 2 TUs limit.
These values show that part of the biocides leach out during EN 84-leaching and harm the *D. magna*. The remaining biocides in the wood blocks are still able to protect the wood effectively against attack by *C. puteana*.

6.3.3 Combining silicones and biocides in wood protection

Figure 6.1 shows that the WPGs of the silicones and the biocide retentions reach the same levels when applied in combination or on their own. Since the solvent-based MTM/n-OTES (S2) is applied at 10 % ai concentration in combination with 1 Wt % Si-Quat it is logic that the obtained WPG is approximately double as high compared to its application at 5 Wt % ai concentration like in all other applications.

The addition of an organosilicon to a biocide containing solution does not have a significant impact on the efficacy in protecting Scots pine sapwood against attack by *C. puteana* (Figure 6.2). Again all mass losses are well below the critical mass loss limit of 3 % and the wood is consequently very durable.

Also the ecotoxicity of the resulting leachates does not differ that much from those of solely biocide-treated Scots pine (Figure 6.3). Indeed, taking the 95 % confidence intervals into account, the same corresponding toxicity is observed for the leachates of Scots pine treated with solely biocides and those treated with a combination of a biocide and an organosilicon. The only exceptions are the 1 day EN 84-leachates of Scots pine sapwood impregnated with water-based IPBC and propiconazole or impregnated with solvent-based IPBC. The first biocide mixture generates higher toxicity and the second biocide lower toxicity when applied in combination with an organosilicon. Once more the ratio

of applied concentration Si-Quat (2/1 % ai) to the wood blocks is roughly equal to the ratio of TUs of the wood leachates (11.4/6.4 TUs). Due to the high toxicities also the 14 days EN 84-leachates and the 1 day OECD part 1-leachates were examined. Although the EN 84-leachate after 14 days of 50 Wt % DMS/n-OTES (S2) plus IPBC (B2) treated wood is still slightly toxic (6.6 TUs), all other leachates have toxicities approximating or lower than 2 TUs. This means that it can be assumed none of the combinations would induce significant toxicity in real life leaching. Therefore it was not considered valuable to evaluate 14 days OECD part 1- leachates.

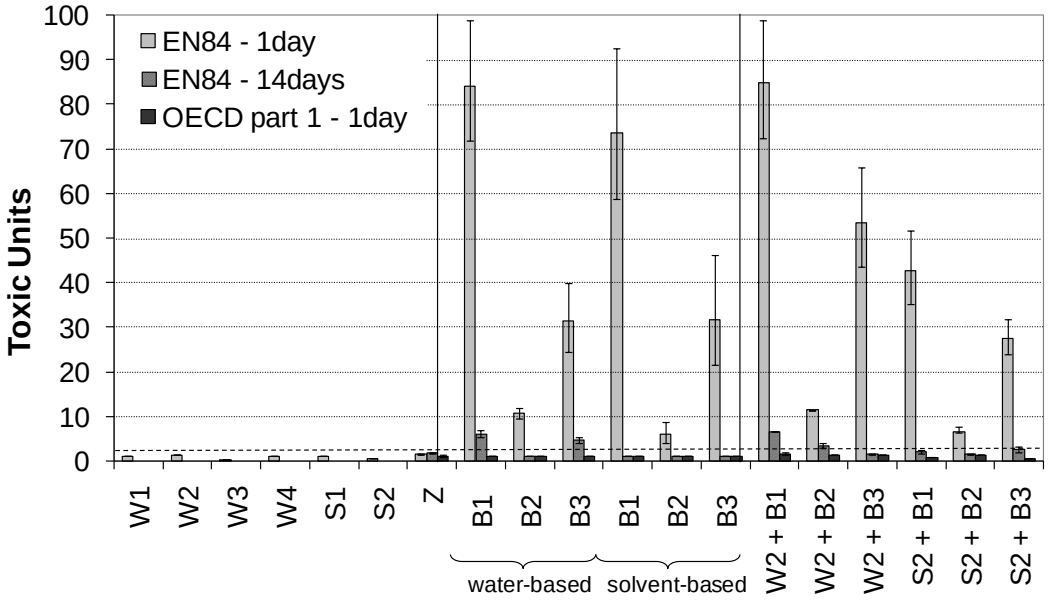

Figure 6.3: Toxic units of different leachates of Scots pine sapwood impregnated with organosilicons, biocides or both. The bars represent the 95% confidence intervals of the toxic units. The dashed line is situated at 2 toxic units

Considering both the toxicities of leachates from wood treated with solely biocides or in combinations with organosilicons, Figure 6.3 shows that the toxicities decrease over time. More precisely the toxicity to *D. magna* after 14 days EN 84-leaching is 3 to 37 times smaller than after 1 day, resulting in <2 to 6.6 TUs after 14 days leaching. Furthermore the toxicity of the OECD part 1-leachates was even lower (<2 TUs). The EN 84-leachates indicate that the solvent-based treatments are less toxic to *Daphnia magna* than their corresponding water-based combinations, regardless the time of harvesting.

6.4 Discussion

Different investigations were undertaken to evaluate the effectiveness of organosilicons in protecting wood from fungal decay. For most treatments no full protection could be guaranteed to the wood when the organosilicons were applied at low concentrations (Goethals and Stevens 1994; Hill et al. 2004; De Vetter and van Acker 2005). Nevertheless some significant protective effectiveness is observed. None of the organosilicons applied at 5 Wt % ai is able to protect the wood up to decay rates below 3 % mass loss. However some treatments can enhance the durability with 1 or 2 classes, making the treated wood suitable for applications under use class 3 conditions. Furthermore the ecotoxicity results are very promising since the values are comparable to the value of untreated Scots pine sapwood leachate, which is considered not to be toxic (De Vetter et al. 2008).

Although the common use of IPBC, limited literature data are available on the required effective concentrations against wood destroying basidiomycetes. Hansen (1984) reported toxic values of IPBC treated Scots pine against *C. puteana* of 0.2-0.4 kg/m³ for unleached and 0.3-0.5 kg/m³ for EN 84-leached EN 113 specimens. Cserjesi et al. (1984) showed that IPBC was ineffective in controlling fungal growth (mould, stain fungi but especially degrading fungi) on spruce-pine-fir lumber dipped in a solution at a concentration as high as 0.8 % active ingredient IPBC. However, in this study quite high concentrations of IPBC were tested. A preservative concentration of approximately 0.3 Wt % ai induced an IPBC retention of about 1.3-2.0 kg/m³. Therefore it is not surprising that the Scots pine is protected effectively against brown rot decay, irrespective the addition of an organosilicon to the treating solution.

Published information on the toxicity of IPBC towards *D. magna* is very scant. While Farrell et al. (1998) found that *D. magna* was the most sensitive species among both invertebrates as well as fishes with an LC_{50} of 40 µg/l IPBC, Henderson (1992) reported a 48-hour LC_{50} as high as 645 µg/l IPBC. This study reports the ecotoxicities of leachates of IPBC treated wood using high

preservative concentrations. It is not surprising that the leachates are toxic and it is clear that lower concentrations of IPBC would still be effective against decay and yield lower toxicity towards *D. magna*.

Donath et al. (2006b) have treated Scots pine and beech mini-blocks with a multifunctional silane alone or in combination with 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride (Si-Quat). After EN 84-leaching the recorded mass losses were about the same, irrespective the addition of the Si-Quat to the treating solutions. They assume that the Si-Quat is either incorporated into the siloxane matrix of the silane or that it is fixed to the wood cell wall. Incorporation of the Si-Quat would prevent mould fungi of being able to degrade quats, a functionality reported by Dubois and Ruddick (1998). Since in this study the same toxicity (and corresponding concentration of Si-Quat) is found for the leachates irrespective the addition of an organosilicon, fixation to the wood cell wall seems the most plausible.

Isquith et al. (1972) demonstrated that the Si-Quat had antimicrobial activity in a serial tube dilution method without entering the cell and attributed this activity to membrane phenomena. Donath et al. (2006b) proved the Si-Quat to be also effective in protecting Scots pine sapwood against fungal decay by *C. puteana* when incorporated in a siloxane matrix. The Si-Quat was applied at a concentration of at least 0.5 % active ingredient in combination with 5 % active ingredient multifunctional silane. In this study such a low concentration was not tested but the full protection reached at 1 Wt % active ingredient Si-Quat suggests that even lower concentrations could suffice to protect Scots pine sapwood effectively against attack by *C. puteana*. Nevertheless, as Briscoe et al. (1990) pointed out for several wood preservatives, the evaluation of a new wood preservative should always include a test using natural mixed microbial populations to see its effectiveness in real exposure conditions.

Toxic values of solvent-based propiconazole for Scots pine EN 113 impregnated specimens against *C. puteana* are determined to be between 0.27-

0.39 kg/m³ ai for unaged specimens and between 0.20-0.31 kg/m³ ai for EN 84-leached specimens (Valcke 1989; Valcke and Stevens 1991). For Scots pine sapwood EN 113 specimens treated with water-based propiconazole and exposed under the same circumstances, toxic values lower than 0.37 kg/m³ ai for unaged specimens and between 0.42-0.60 kg/m³ ai for EN 84-leached specimens are found (Buschhaus and valcke 1995). However, Valcke and Stevens (1991) pointed out that an equal or preferentially a higher loading at the outermost shell of EN 113 specimens is necessary to protect the wood effectively against fungal attack, and this especially when the wood is treated superficially. In this research a combination of 0.6 Wt % ai propiconazole and 0.3 Wt % ai IPBC protects the wood sufficiently, irrespective the solvent used (water or IPA) or the addition of 5 Wt % ai organosilicon. It was shown before that leaching and evaporative ageing did not have a negative impact on the protective effectiveness of propiconazole (Valcke 1989; Valcke and Stevens 1991).

Propiconazole is one of the best characterized chemicals interfering with the embryonic development of *D. magna*, although up to now only acute toxicities of the chemical itself are reported (Wegens 1991; Soetaert et al. 2006). Since in the present research propiconazole was combined with IPBC and no chemical analyses on the leachates were performed no exact toxicity values can be calculated for propiconazole. However, it was observed that Scots pine treated with a combination of IPBC and propiconazole yields lower leachate toxicities than when Scots pine is treated with the same concentration of solely IPBC. Although it has been reported before that the formulation type has a major impact on the final result (Valcke 1989), in this research only minor effect of the solvent was noticed. At the concentrations mentioned before, wood is protected effectively against fungal decay, but high leachate toxicities are recorded. It is therefore suggested to lower the amount of product applied, which might also lead to some significant impact on leached fungicides when organosilicons are added.

6.5 Conclusion

As a final conclusion it can be postulated that organosilicons applied at low concentrations are not able to protect Scots pine sapwood specimens fully from fungal decay and that their leachates are not harmful to the crustacean *D. magna*. Biocide-treated Scots pine specimens are protected effectively against fungal attack, but their leachates yield a high toxicity towards *D. magna*. This ecotoxicity level depends both on the preservative and concentration applied. Combining the organosilicons and biocides in the treating solution does not change the protective effectiveness of the treated wood, but does not reduce the toxicity of their leachates either. These observations are valid both for water-based and solvent-based impregnating solutions. The authors would like to stress that this conclusion is valid for the test set-up as described in this research: using a high amount of biocide and only a small amount of organosilicon. To lower the toxicity towards *D. magna* a lower amount of biocide is desirable. Since the mass loss results for fungal testing are well below 3 % this might still be effective against fungal attack. Whether under these circumstances a higher amount of silicones would be effective in preventing leaching should be further investigated. Nevertheless also economic constraints related to the addition of the organosilicons should be considered.

However, this does not mean that adding an organosilicon to a biocide containing treating solution could not have an added value. The organosilicons may have a positive effect on the wood-moisture relationship reducing moisture related damage like surface erosion, defibrillation, crack formation etc. of the wood and thereby contributing to a longer service life of the treated wood.

Acknowledgements

We would like to express our gratitude to Dow Corning Corporation for supplying the organosilicons and to Troy Corporation, AEGIS Environments Inc. and Janssen Pharmaceutica nv for providing the biocides. The authors are grateful to the European Commision for funding the Research Project

‘Improvement of Wood Product Properties by Increased Hydrophobicity Obtained by the Use of Silicon Compounds’ - HYDROPHOB (QLK5-CT-2002-01439), which was the framework for this study.

Discussion

First of all it was found that organosilicons are able to protect wood from fungal decay at very high concentrations. Since it was the purpose of this dissertation to focus on economically feasible concentrations it had to be concluded that organosilicons could induce an improvement, which was only in a minority of cases sufficient to protect wood focussing on outdoor, out of ground use.

Under these exposure conditions however, not only the efficacy but also the ecotoxicity of the leachates plays an important role in the approval of the treatment. Therefore a study was performed on methodology how to combine these two parameters. For this study usage was made of wood treated according to known methods, like wood preservation and wood modification. The methodology as described above proved to be suited for both product groups but also pointed towards the difficulty in finding an acceptable balance between the two parameters. Although not always the case, an improvement in one parameter often worsened the other, and vice-versa.

Subsequently this method was used to evaluate organosilicon treated wood. Since it was found that organosilicons as such would probably not suffice to protect the wood adequately, combinations with biocides were sought. Moreover the hypothesis was tested whether organosilicons would be able to reduce leaching of these biocides, which have known fungal effectiveness. The methodology was found suited for testing the organosilicon (and biocide) treated wood, but showed that organosilicons could not reduce biocide-leaching.

Taking all this information into consideration it was found necessary to do more research on the wood-water relationship, since this might be the key aspect in the mode of action of organosilicons applied onto wood. In the laboratory basidiomycetes testing this factor is ruled out, because high moisture contents are forced to the treated wood, due to the set-up of the experiments. This wood-water relationship is the subject of the next part of this dissertation.

PART III

MOISTURE DYNAMICS AS BASIS FOR PERFORMANCE OF ORGANOSILICON WOOD TREATMENTS

Preface

Wood is a three dimensional structure mainly composed of cellulose, hemicellulose and lignin. These molecules all have hydroxyl groups available to which water can bond. When water bonds to these groups, certain features of the wood change, going from its dimensions to its characteristics like strength, colour, etc. The presence of moisture in wood is however also the triggering factor for most fungi to feed onto wood, leading to wood degradation and failure of for example a construction element. It is therefore not surprising that most of these moisture induced changes of wood are not appreciated by end-users. That is why measures are undertaken to avoid or diminish the impact of water on wood. Proper design of the wooden element is a first measure which can be taken.

More often positive action is searched by treating wood with a water repellent. Different groups of chemicals have been applied for that purpose. Organosilicons proved their effectiveness as water repellents on many other materials, like the mineral construction materials concrete, mortar and cement. Application of these products onto wood using the knowledge gained on mineral substrates led to some disappointing results. It was soon found out that wood, with its three dimensional, non homogeneous and non-reactive structure is far more complicated to treat effectively.

Previous chapters have revealed that organosilicons as such cannot provide the desired effectiveness against fungal attack when applied at low concentrations. Hence the organosilicon treated wood was not similar to preservative treated or durable wood. This does not mean that organosilicons do not interact with wood at all, but that the interaction is not such that protection is guaranteed. Knowing that a minimal amount of water is needed by most fungi to degrade wood, interfering in the wood-moisture relation might indirectly influence the interaction between wood and fungi.

How this effect should be tested is not straighforward. Laboratory tests were developed to simulate certain exposure conditions and gain fundamental insight on how the wood would behave once treated. Through experience however it must be concluded that a big discrepancy can be present between these laboratory tests and real outdoor exposure. Therefore performance testing, putting small-scaled elements outside, are often a better way to go for. Unfortunately they have the disadvantage to be dependent on surrounding circumstances like location and climatic conditions and require a significant longer test period.

When one thinks of applying wood outside, most customers have a certain image of how it should look once installed and how it should look in ten years' time. However, weathering of wood surfaces leads to cracks, surface roughness, fungal growth and colour changes due to UV radiation. Although

these are hard to predict for wood it is interesting to investigate possible disfigurement of the wood surface.

In the next part different aspects of the wood-water relationship are evaluated and this under varying laboratory conditions onto both solid wood and wood flour as well as on wood-based and re-engineered materials. Since laboratory conditions cannot exactly mimic real outdoor exposure and its changing character, additional outdoor performance testing was considered indispensable. These tests focus on application outside, out of ground contact. Besides cladding and its possible disfigurement also low quality window corners were exposed simulating worst case conditions.


DYNAMIC VAPOUR SORPTION

7 IMPACT OF ORGANOSILICON TREATMENTS ON THE WOOD-WATER RELATIONSHIP OF SOLID WOOD[1]

Abstract

Organosilicons are proposed as protecting agents for wood used outdoors. In these outdoor applications, the interaction of the wood with water is of primary importance. That is why in this research the influence of water on organosilicon treated material was investigated. In this first part solid Scots pine sapwood was impregnated with or submerged into low concentrations of organosilicons and evaluated for several water related characteristics. None of the examined properties was significantly different between untreated and organosilicon treated wood, leading to the conclusion that application of organosilicons to wood cannot be regarded as wood modification in the strict sense. Whether higher concentrations would lead to better performance is investigated in the second part of the study.

[1] In preparation for Holzforschung as:
De Vetter, L., Van den Bulcke, J. Stevens, M. and Van Acker, J. Impact of organosilicon treatments on the wood-water relationship. Part I: Treatment of solid wood with low concentrated organosilicons.

7.1 Introduction

Wood used outdoors is prone to physical, chemical as well as biological degradation. The susceptibility to fungal decay of outdoor wooden constructions greatly depends on the moisture content. Therefore, efforts are undertaken to reduce this moisture content and keep it below the critical value of circa 20 %. One way is modifying the wood properties by chemical, thermal, surface or impregnation modification (Hill 2006). Organosilicons may be used as impregnates and have shown modification efficiency in several industrial applications, like concrete, brick and stone protection and in the textile, paper and plastics industries.

Efforts were undertaken to evaluate their efficacy as protecting agents of wood (Goethals and Stevens 1994; Donath et al. 2004; Mai and Militz 2004b, Weigenand et al. 2007). At the one hand it was already proven that they have a limited effect in protecting wood from fungal degradation (De Vetter et al. 2009b), while at the other hand it was suggested that organosilicons might protect wood in outdoor conditions (Lukowsky and Peek 1997; Mai and Militz 2004b; Donath et al. 2006; De Vetter et al. 2009a). Because in the available literature different wood species, impregnation solutions, treating parameters, testing protocols and evaluation parameters are used it is hard to get a uniform picture of the moisture behaviour of organosilicon treated wood.

While it was found that silanes do not considerably lower the equilibrium moisture content (Goethals and Stevens 1994) or lead to improved dimensional stability (Donath et al. 2004), it was observed that they have a positive effect on water repellence (Donath et al. 2006a). Hager (1995) reported a reduction of the water uptake of silicone treated spruce by 70 %, while silicones could not obtain significant anti swelling efficiency (ASE) in another study (Lukowsky and Peek 1997). Furthermore only moderate ASE and reduction in water uptake was reported for silicone impregnated Scots pine sapwood (Weigenand et al. 2007).

It was shown before that organosilicons can succesfully be applied to protect wood from fungal degradation, but only at high concentrations which are no longer considered economically feasible (De Vetter et al. 2009b). It was found interesting to investigate whether the same is true for protection against moisture uptake. Therefore the influence under laboratory conditions of organosilicons applied at low concentrations onto solid wood was investigated.

7.2 Materials and methods

7.2.1 Chemicals

This research covers several tests to get a global picture of the behaviour of organosilicon treated wood in contact with water, including both liquid water and water vapour. In total seven different organosilicon formulations were used. Due to an increased awareness of the environmental impact of solvent-based products, more environmentally friendly aqueous solutions were developed by the industry. That is why in this research five water-based products and only two solvent-based products were included. Among the water-based systems there was one micro-emulsion W4 (Wacker-Chemie GmbH, Germany), having particle sizes which are a lot smaller than those of the macro-emulsions. It is assumed that these smaller particles penetrate deeper into the wood matrix than the conventional emulsions (Mai and Militz 2004b). The water-based silicone (micro)emulsions (W1 → W5) all contain the components (poly)dimethylsiloxane ((P)DMS) and/or (N-octyl)triethoxysilane ((n-O)TES), yet with different end groups and in changing active ingredient concentrations ranging from 40 % to 100 %. The two solvent-based products (S1 and S2) are 100 % active and have as main components the alkoxysilanes OTES and/or methyltrimethoxysilane (MTM). All products, except for the micro-emulsion W4, were supplied by Dow Corning Corporation (Seneffe, Belgium). More information on these products can be found under heading 1.3.1.

7.2.2 Wood materials and treatment procedures

For all tests Scots pine sapwood (*Pinus sylvestris* L.) was used, although in the water uptake and vapour uptake tests also beech (*Fagus sylvatica* L.) was included. For the dynamic vapour sorption (DVS, Surface Measurement Systems) test part of the solid treated wood was milled to wood flour.

Depending on the test method different application strategies were used such as vacuum impregnation and submersion/dipping. Regardless the application method, all specimens were conditioned prior to application at 20 °C and 65 % relative humidity (RH). The exact vacuum impregnation and submersion procedures have been explained before (section 1.3.2). The products were diluted to a concentration of 5 % active ingredient. Solvents used were water for the aqueous systems and isopropylalcohol for the solvent-based systems. All specimens were weighed prior to and after application allowing calculation of the uptake of product, expressed as weight percent gain (WPG, Eq. 1.1) for the impregnated specimens and in g/m^2 for the dipped specimens (Eq. 1.4).

7.2.3 Moisture dynamics of organosilicon treated solid wood

In this part of the research focus was on the evaluation of organosilicons applied at low concentrations onto solid wood. Therefore four different test set-ups were delineated. Firstly small (30 × 30 × 5 mm, R × T × L) Scots pine sapwood and beech specimens were vacuum impregnated with 5 % concentration of W1, W2 or W3. After drying at 60 °C the specimens were impregnated in the same way with water as explained before (1.3) and afterwards dried at 60 °C. At each of these stages the mass, radial and tangential dimensions of each block were determined. Since it is known that longitudinal swelling is negligible compared to radial and tangential swelling, the volumetric swelling S of the blocks can be calculated based on the surface area A of each block at the different stages (Van Acker 2003). Consequently the anti swelling efficiencies (ASEs) and anti shrinkage efficiencies (AsEs) can be calculated based on equations 7.1 to 7.4.

$$S_{swell}\ (\%) = \frac{A_{wet}(mm^2) - A_{dry}(mm^2)}{A_{dry}(mm^2)} \quad (7.1)$$

$$S_{shrinkage}\ (\%) = \frac{A_{wet}(mm^2) - A_{dry}(mm^2)}{A_{wet}(mm^2)} \quad (7.2)$$

$$ASE\ (\%) = \frac{S_{swell\_untreated}\ (\%) - S_{swell\_treated}\ (\%)}{S_{swell\_untreated}\ (\%)} \quad (7.3)$$

$$AsE\ (\%) = \frac{S_{shrinkage\_untreated}\ (\%) - S_{shrinkage\_treated}(\%)}{S_{shrinkage\_untreated}\ (\%)} \quad (7.4)$$

The water repellent effectiveness (WRE) on the other hand, is calculated based on the relative water uptake (RWU) using the masses of the specimens following equations 7.5 and 7.6. Since these steps were repeated three times three ASEs, AsEs and WREs could be calculated. Although the cyclic vacuum impregnation/oven drying test is not representative for the in-service expansion of wood, it simulates the maximum potential swelling which may occur (APA No. TT-028 1994).

$$RWU\ (\%) = \frac{m_{wet}\ (g) - m_{dry}(g)}{m_{dry\_untreated}(g)} \times 100 \quad (7.5)$$

$$WRE\ (\%) = \frac{RWU_{untreated} - RWU_{treated}}{RWU_{untreated}} \times 100 \quad (7.6)$$

Besides this first so-called water uptake test including consecutive water impregnations and drying of the specimens, an analogous vapour uptake test was performed. In this test water vapour instead of liquid water is used to swell and shrink the wood. More precisely were the specimens conditioned in a climate chamber at 20 °C and RH equal to 60 % or 90 %. This means that the physical parameters mass and area during dry conditions were those at 60 % RH, while the wet conditions corresponded to 90 % RH.

Besides this static water vapour uptake, action was undertaken to determine the dynamic vapour sorption of treated Scots pine sapwood. Therefore specimens (30 × 30 × 5 mm, R × T × L) were vacuum impregnated with 5 % active ingredient concentration of products W2, W3, W4, W5, S1 or S2. After drying a

small subsample (4 × 4 × 5 mm, R × T × L) was cut out of every specimen, while the remainders were milled (sieve 1 mm) to wood flour. Both the solid cubes (masses between 43.2 g and 58.4 g) and wood flour (ranging from 45.3 g to 48.4 g) of each treatment were brought in a dynamic vapour sorption (DVS) device. The main component of the DVS system is an ultra-sensitive recording microbalance housed in a controlled constant temperature incubator and capable of measuring changes in sample mass lower than 1 part in 10 million. For this test the temperature of the sample region was fixed to the same temperature of the microbalance region, namely 25 °C. The humidity in contrast ranged from 0 % RH to 90 % RH and was generated by mixing dry and saturated vapour gas flows using mass flow controllers. The sample was given the time to dry and reach equilibrium at 0 % RH. When dm/dt was less than 0.002 g/s or after at maximum 240 min the RH was raised in steps of 10 % RH to 90 % and then in steps of 10 % RH downwards. The specimens were given 60 min to adapt to each new RH. The weight of the specimens was determined throughout the whole test and the mass change can be plotted against time.

In the last test set-up a combination of water sorption and vapour sorption was simulated by exposing Scots pine sapwood samples to artificial weathering. In this test the front side of the test specimens was sprayed with water, while the back side of the specimens was exposed to the resulting high relative humidity. The specimens (40 × 10 × 320 mm, R × T × L) were submerged into a 5 % concentration of the products W2, W3, W4, W5, S1 or S2, after both cross cuts had been sealed with two coats of a water-impermeable two-component polyurethane system. The specimens were reconditioned at 20 °C and 65 % RH after which they were mounted on the artificial weathering machine ATLAS UVCON (UV cabinet with spray option). This machine contains a fluorescent black light with peak emissions of 340-370 nm, programmable water spray nozzles, irradiance control and a black panel thermometer. The weathering cycles were alternating a wetter and dryer cycle, The first so-called wet cycle consisted of an illumination during 23 hours, followed by a dark period of one hour. In the mean time, spray nozzles were turned on and off according to the

left diagram showed below (Figure 7.1). After six days the specimens were put in the refrigerator at 4 °C during 24 hours. The next week, a dry cycle B was performed under continuous illumination. The wetting cycle is shown below on the right pie. After six days the specimens were again removed from the weathering machine and put in the freezer at -8 °C for 24 hours. The third week cyle A was started again and the last week cycle B was performed. After each of these four cycles the masses of the specimens were determined, allowing calculating the moisture content (MC) at time t according to equation 7.7.

$$MC_t\ (\%) = \frac{m_t\,(g) - m_{103°C}(g)}{m_{103°C}(g)} \times 100 \qquad (7.7)$$

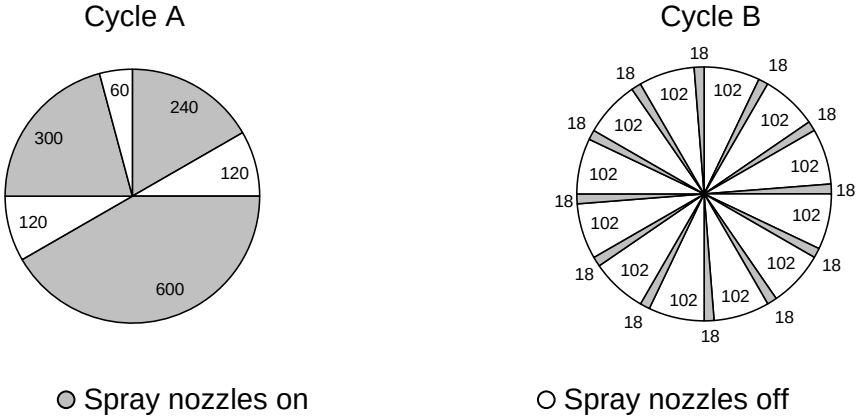

Figure 7.1: Spray nozzle cycles during 24 hours weathering in an ATLAS UVCON (minutes)

7.3 Results

Tables 7.1 and 7.2 give an overview of the obtained WPGs of the vacuum impregnation and of the WREs, ASEs and AsEs during each of the three consecutive wet and dry cycles of both the water uptake test and vapour uptake test for Scots pine sapwood and beech, respectively. These tables show that concerning the water uptake test none of the products is able to induce any significant change in WRE, ASE or AsE, and this for both wood species. For the vapour uptake test the treatment of beech with product W1 catches the eye,

since it is the only combination which leads to both ASE and AsE values higher than 15 % for all three cycles. In contrast the corresponding WRE is not influenced a lot.

Table 7.1: Weight percent gain (WPG), water repellent effectiveness (WRE), anti swelling efficiency (ASE) and anti shrinkage efficiency (AsE) of Scots pine sapwood during three consecutive cycles of the liquid water uptake and water vapour uptake tests

Product	Cycle	Water uptake				Vapour uptake			
		WPG (%)	WRE (%)	ASE (%)	AsE (%)	WPG (%)	WRE (%)	ASE (%)	AsE (%)
W1	1	5.51	3.19	-3.31	-0.22	6.00	-6.10	9.17	-1.49
	2		2.47	0.50	-0.93		-22.29	3.39	-0.98
	3		2.11	-1.28	-0.21		-11.27	-8.07	3.23
W2	1	5.78	7.71	-1.28	0.37	5.90	0.05	2.66	-2.44
	2		4.29	-0.14	-0.65		-19.23	-9.43	-12.38
	3		4.72	-0.04	0.13		-7.31	-11.76	-2.88
W3	1	5.56	3.83	-1.95	0.10	6.12	11.00	9.56	12.72
	2		2.13	0.52	0.82		-13.87	-3.51	-5.5
	3		3.42	1.12	1.24		1.00	-1.43	10.72

Table 7.2: Weight percent gain (WPG), water repellent effectiveness (WRE), anti swelling efficiency (ASE) and anti shrinkage efficiency (AsE) of beech during three consecutive cycles of the liquid water uptake and water vapour uptake tests

Product	Cycle	Water uptake				Vapour uptake			
		WPG (%)	WRE (%)	ASE (%)	AsE (%)	WPG (%)	WRE (%)	ASE (%)	AsE (%)
W1	1	4.4	8.2	8.5	-1.8	4.6	11.6	22.9	30.4
	2		8.5	-1.2	-1.5		-1.1	17.8	15.2
	3		6.2	-0.5	0.2		-3.3	16.5	20.8
W2	1	4.3	8.5	9.3	0.6	4.1	3.3	8.5	3.9
	2		6.3	2.4	2.1		-7.3	-0.0	-1.3
	3		5.4	3.1	4.0		-8.3	-4.4	-6.9
W3	1	4.6	8.2	8.6	-0.5	4.1	-1.1	2.3	-1.9
	2		5.9	1.1	-0.3		-2.6	1.6	-0.2
	3		5.9	0.2	0.6		-1.7	-0.3	0.3

Figures 7.2 and 7.3 show the resulting graphs of the percentage mass change induced during the dynamic vapour sorption test of the solid wood and the wood flour, respectively. None of the wood blocks or flours reached equilibrium

moisture content within 240 min, meaning dm/dt is still higher than 0.002 g/s. Nevertheless the mass changes were very low after 240 min, especially for the wood flours. These so-called dry masses after 240 min were set at 100 %. Minor differences exist among the different treatments in the speed at which they react on changing RH and the corresponding equilibrium moisture content, as far as it is reached within 60 min. However, no real major differences among the treatments and in comparison to untreated Scots pine sapwood can be seen. The only noticeable difference is that wood flour reacts faster than solid wood on changing RH and has a higher sorption and desorption of moisture. The hysteresis in contrast, was comparable (data not presented).

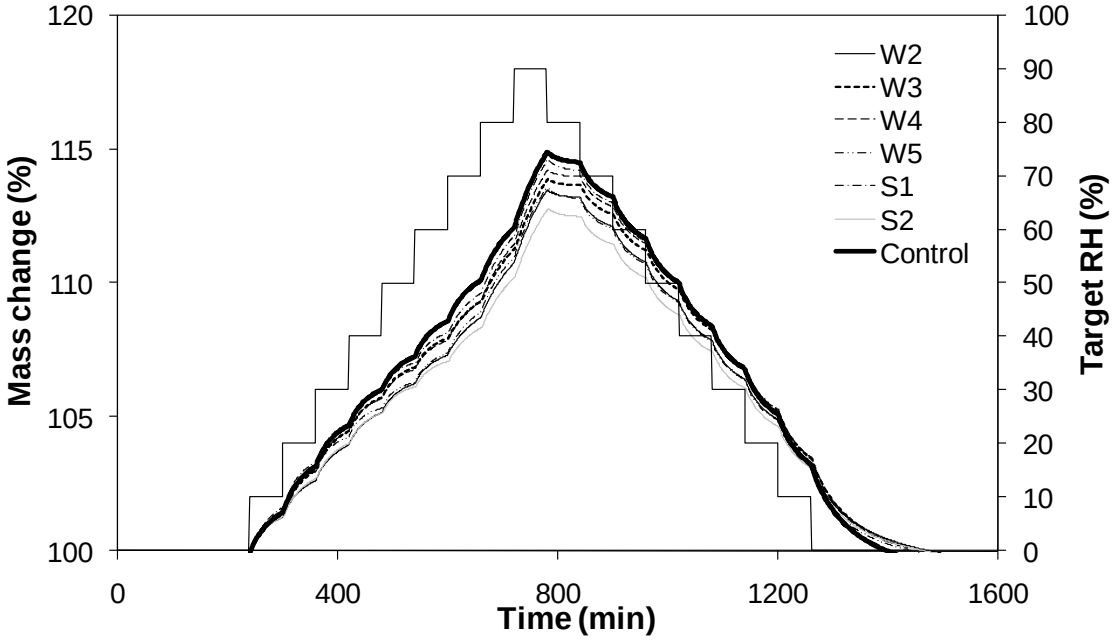

Figure 7.2: Mass change versus time of untreated and organosilicon treated solid Scots pine sapwood during a dynamic vapour sorption test

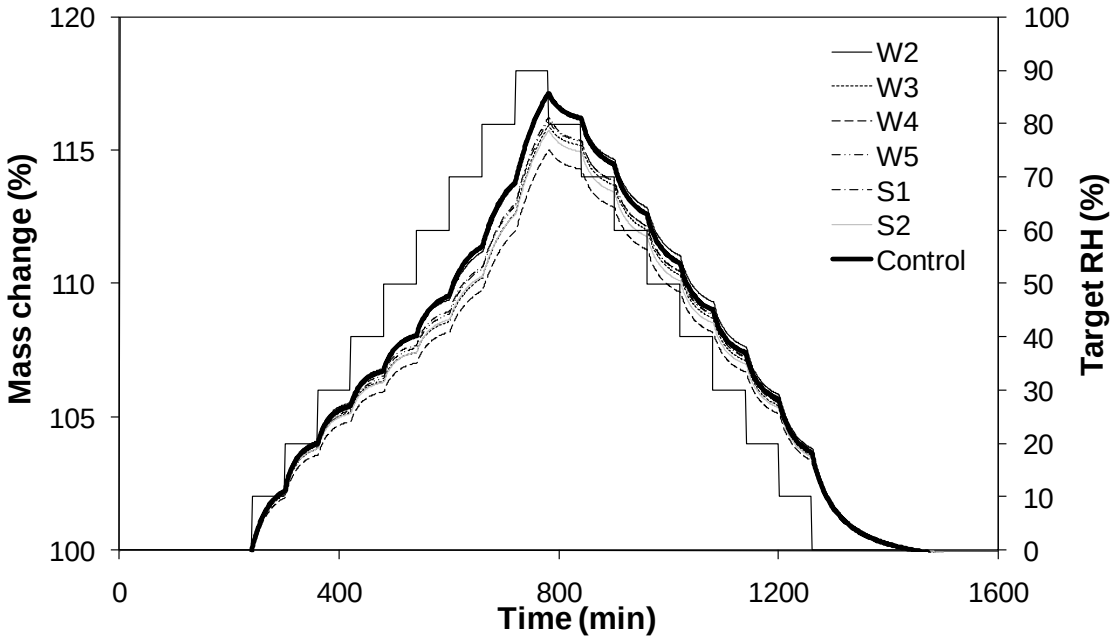

Figure 7.3: Mass change versus time of milled untreated and organosilicon treated Scots pine sapwood during a dynamic vapour sorption test

Finally, the moisture content of both organosilicon treated as well as untreated Scots pine sapwood after each of the four artificial weathering cycles is presented in Figure 7.4, while Table 7.3 gives the product retentions. No significant differences among the moisture contents can be observed, although after cycles 3 and 4 some minor differences are noticeable.

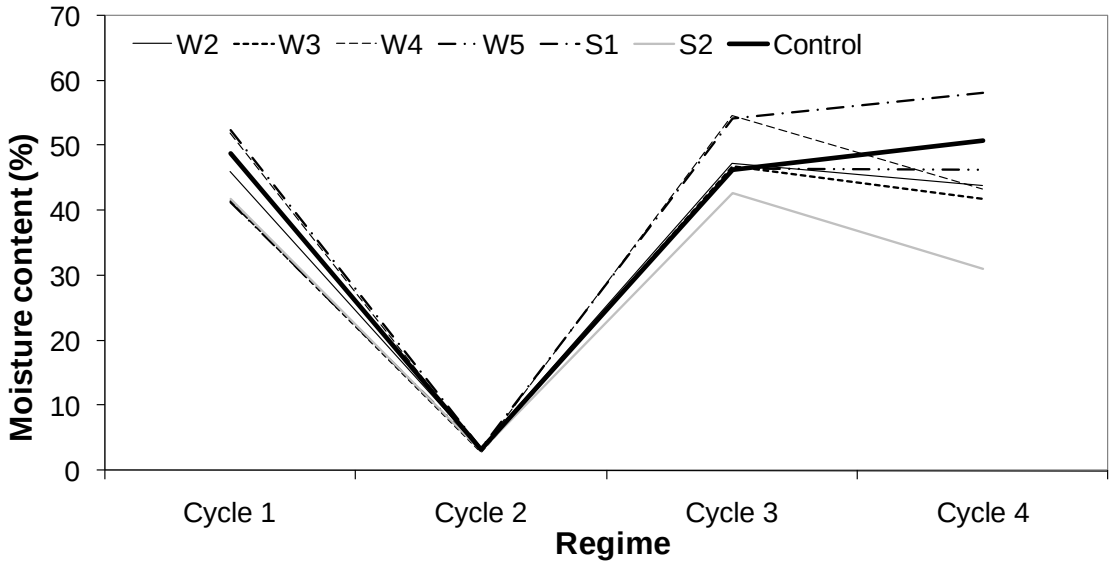

Figure 7.4: Change in moisture content of organosilicon treated wood during consecutive cycles of artificial weathering

Table 7.3: Product retention (g/m^2) of Scots pine sapwood impregnated with 5 % active ingredient concentration of different organosilicons

Organosilicon	Product retention (g/m²)
W2	7.8 ± 1.8
W3	6.8 ± 2.0
W4	3.3 ± 1.3
W5	2.7 ± 0.8
S1	2.3 ± 0.9
S2	2.3 ± 0.9

7.4 Discussion

Goethals and Stevens (1994) have put beech and Scots pine sapwood impregnated with propyltrimethoxysilane through multicycle water soaking/drying tests and water vapour sorption tests. Although beech and Scots pine was treated at 11.5 % and 24.4 % WPG, an average anti shrinkage efficiency over 5 cycles of only 35 % and 27 % was reached. Also the water vapour tests could not reveal any decrease in hygroscopicity. Furthermore Donath et al. (2004) could only find a slight reduction in moisture uptake when silane treated beech was exposed to various humidity conditions and ASE values up to 30 % were reported. For both parameters the best results were noted when the organosilicons were applied in the silane state instead of the sol state. However, regardless the application state, the positive effects diminished considerably after ageing.

Weigenand et al. (2007) recorded low ASE and WRE values for Scots pine sapwood impregnated with macro- or micro-amino-silicone-emulsions when submerged in tap water, especially when the corresponding high WPGs were taken into consideration. Donath et al. (2006a) in contrast showed high water repellence of silane treated wood, especially after treatment with multifunctional water-based silane systems containing both hydrophilic and hydrophobic groups. The high water repellence of silane treated wood was also confirmed in

weathering tests, albeit only a small change of sorption behaviour was recorded (Donath et al. 2007).

Although the testing procedures and calculation methods used to determine WRE are very diverse, the general conclusion seems to be that organosilicons can improve the WRE, but lose their effectiveness greatly due to leaching. In the first part of this research, where organosilicons were applied onto solid Scots pine sapwood, no evidence could be found of improved ASE, AsE, WRE or moisture uptake values. However, the applied WPGs were lower than those reported in the literature as mentioned above.

Hill (2006) defines wood modification as a process altering the properties of wood permanently so that no loss of the enhanced performance occurs during lifetime of the wood. Common conclusion of the results found in this research and literature leads to the finding that treatments of solid wood at low to moderate WPGs of organosilicons does not fulfil this requirement and can therefore not be regarded as wood modification. Nevertheless do most authors conclude that there is a potential to use organosilicons for the protection of wood used outdoors (Lukowsky and Peek 1997; Donath et al. 2006a). This line of thinking is the subject of further research (Chapters 9 and 10).

Since it has been shown before that the acceptance of a certain water repellent formulation may depend on the test parameter chosen (Nussbaum 1989), it is advised to perform several test set-ups. These tests should not only include smaller and bigger specimens, but should besides laboratory tests also be complemented with field experiments. That is why the results of this study should be interpreted in their proper context, namely as laboratory tests. Before extrapolating the results to outdoor exposures they need to be completed with field test experiments. To meet these needs contact angle measurments are being performed on naturally and artificially weathered Scots pine sapwood specimens. Upon availability of these results, they will be checked with above mentioned findings.

7.5 Conclusion

Underlying study found only small to no significant change in the wood-water related properties anti swelling efficiency, anti shrinkage efficieny, water repellent effectiveness or (equilibrium) moisture content when solid Scots pine sapwood or beech was impregnated or submerged in low concentrated organosilicons. Moreover this research confirmed that vacuum impregnation of solid wood with organosilicons cannot be regarded as impregnation modification of wood, since no permanent change in the tested properties could be found.
However, this does not exclude that application of higher concentrations of organosilicons would not be able to induce changes in the wood-water relationship. This is subject of the second part of this research (Chapter 8).

Acknowledgements

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8 IMPACT OF ORGANOSILICON ENVELOPE TREATMENTS ON THE WOOD-WATER RELATIONSHIP OF WOOD-BASED MATERIALS[1]

Abstract

Due to the hygroscopicity of wood several wood related properties are influenced by the moisture content of the wood. Especially when wood is being used outdoors, out of ground contact, the interaction with water is important. In a first part of this study it was found that low concentrated organosilicon treatment of solid wood did not lead to significant improvement of wood-water related properties. This part of the research therefore focuses on highly concentrated organosilicons applied to the envelope of wood materials. Not only solid wood but also plywood, medium density fibreboard (MDF) and oriented strand board (OSB) were considered. Superficial application shows potential in protecting solid wood and plywood. Drawback is reduced effectiveness of the organosilicons due to weathering. Negative results were obtained for organosilicon treated MDF and OSB. To fundamentally explain the different behaviour between various wood products further research has to be conducted.

[1] In preparation for Holzforschung as:
De Vetter, L., Stevens, M. and Van Acker, J. Impact of organosilicon treatments on the wood-water relationship. Part II: Envelope treatment of wood-based materials with highly concentrated organosilicons.

8.1 Introduction

Not only solid wood, but also wood-based products or re-engineered wood products benefit from protective measurements when exposed outside. One way of protecting the wood is by lowering its ability to take up liquid water or water vapour. This can be done by modifying the wood, making it less hydrophobic or by creating a protective envelope around the wood, inhibiting moisture to reach the wood easily.

Since organosilicons are hydrophobing agents, they are supposed to interact in the wood-water relationship, leading to lower moisture contents of the wood products. This on its turn should be beneficial for the service life of the wood. Donath et al. (2006a) reported that silanes have a positive effect on water repellence and Hager (1995) found a reduction of water uptake of 70 % for silicone treated spruce. However, in a first part of this research (Chapter 7) it was already demonstrated that application of organosilicons at low concentrations onto wood do not lead to significant improvements of the water related aspects. Recalling that highly concentrated impregnation of solid wood with organosilicons was not considered economically feasible (De Vetter et al. 2009b), it was chosen to treat only the envelope of the wood material with highly concentrated organosilicons.

Although moisture related properties of wood-based products and re-engineered materials and the effects of envelope treatments on them have been investigated before, no literature was found concerning the influence of organosilicons as envelope treatments on these building materials. It was therefore considered valuable to investigate whether organosilicons, when applied at high concentrations, could induce a change in the wood-water relationship. Since under use class 3 conditions not only solid wood, but often wood-based products are being used, several representatives of these product groups were included in the research.

8.2 Materials and methods

8.2.1 Products and treatments

While in the first part of this research (Chapter 7) the five water-based organosilicons W1, W2, W3, W4 and W5 were used, a sixth product W6 composed of 40 % active octyltriethoxysilane (n-OTES) was added. Organosilicon W1 was no longer included in this part of the study. The other water-based organosilicons W2 to W5 were the same and thus contained (poly)dimethylsiloxane ((P)DMS) and/or (N-octyl)triethoxysilane ((n-O)TES), each with different end groups. Organosilicons W2 and W6 were 40 % active, while W3 and W5 were 60 % active. The 100 % active micro-emulsion W4 was composed of polydimethylsiloxane and triethoxysilane (PDMS/TES). Besides the water-based products, also two 100 % active solvent-based products containing either solely n-OTES (S1) or n-OTES in combination with methyltrimethoxysilane (n-OTES/MTM) (S2) were applied. More information on these products can be found in section 1.3 of this work.

All products were obtained from Dow Corning Corporation (Seneffe, Belgium), except for the micro-emulsion W4 which was purchased from Wacker-Chemie (GmbH, Germany). To obtain highly concentrated envelope treatments, the products were brushed twice as supplied (without dilution) onto the wood substrates. Weighing the specimens prior to and after brushing yields the product retention (Eq. 1.4).

As test substrates besides solid Scots pine sapwood four kinds of plywood and re-engineered materials like medium density fibreboard (MDF) and oriented strand board (OSB) were included. The plywoods were made of poplar (11 plies, 15 mm thick), spruce (5 plies, 15 mm thick), birch (11 plies, 15 mm thick) and maritime pine (7 plies, 17 mm thick). All plywoods were glued with phenol formaldehyde, except the poplar plywood which was glued with urea fortified melamine formaldehyde.

8.2.2 Moisture dynamics of envelope treated material

Floating test – envelope experiment

In this part of the research emphasis was on the behaviour of organosilicons applied at high concentrations onto solid wood, wood-based materials and re-engineered wood products. Firstly the organosilicons W2, W3, W4, W5, W6, S1 and S2 were brushed twice as supplied onto Scots pine sapwood (40 × 15 × 320 mm, R× T × L). OSB (18 mm thick) was brushed twice with W2 or W4, while the plywoods were only treated with organosilicon W2. All boards and half of the Scots pine sapwood specimens were conditioned at 20 °C and 65 % RH, while the other half of the Scots pine sapwood specimens was brought to fibre saturation point prior to application. After application the masses of the reconditioned (20 °C, 65 % RH) specimens were determined, after which the specimens (sealed at all edges) were floated onto demineralised water. At fixed intervals up to four hours the increase in mass was recorded, after the specimens had been blotted on drying tissue. Finally the specimens were removed from the water and put with their longest coated face onto a rack, allowing desorption to occur.

Prior to weathering of the specimens in the weathering machine ATLAS UVCON, the masses of the specimens were determined after one night desorption. Since Mukhopadhyaya et al. (2002) proved that the liquid moisture coefficient of wood (eastern white pine) is temperature dependent; all handling was performed in a conditioned room (20 °C, 65 % RH). The first weathering cycle was a so-called wet cycle A, after which the specimens were subjected to a second floating test, followed by a dry cycle B and consecutively a third floating test. This process of alternating floating and weathering was performed several times, depending on the treated material (see further). More information about the water spraying regime and illumination of the specimens during the so-called wet and dry cycles is given in the first part of this research (Chapter 7). It must be noted that the specimens were not put neither in the refrigerator nor in the freezer for 24 hours, but subjected to floating instead. This floating test consisted of 4 hours sorption, followed by 20 hours desorption under

conditioned circumstances. The specimens were weighed after 5s, 5, 10 min, 1, 2, 4, 5 and 24 hours, allowing to calculate the moisture content at each time (Chapter 7, Eq. 7.7).

Imbibition test – concentrated edge experiment

Supplementary to this transverse water sorption and desorption an imbibition test was performed using a concentrated edge treatment. In this test set-up out of at least three MDF boards (15 mm thick), three OSB boards (18 mm thick) and three boards of the four different kinds of plywood (15 or 17 mm thick) small blocks were sawn which were 15 mm wide and 50 mm long (Figure 8.1). As reference, Scots pine sapwood specimens (15 × 15 × 50 mm, R × T × L) were included. Lukowsky et al. (1998) proved that sealing the edges of solid wood blocks or treating them with a water repellent prevented superficial creeping. Therefore water penetrated the samples only via the areas in direct contact with the water. Since it was the purpose to simulate full size boards and evaluating the protective effectiveness of the water repellents only on the exposed side, the surfaces belonging to the original top and bottom side of the boards and the two small end sides (15 × 15 mm) of each block were sealed with two coats of a white two-component polyurethane system. The top of each block was not sealed, to avoid build-up of entrapped air pressure which might slow down the water absorption (Candanedo and Derome 2005)(Figure 8.1).

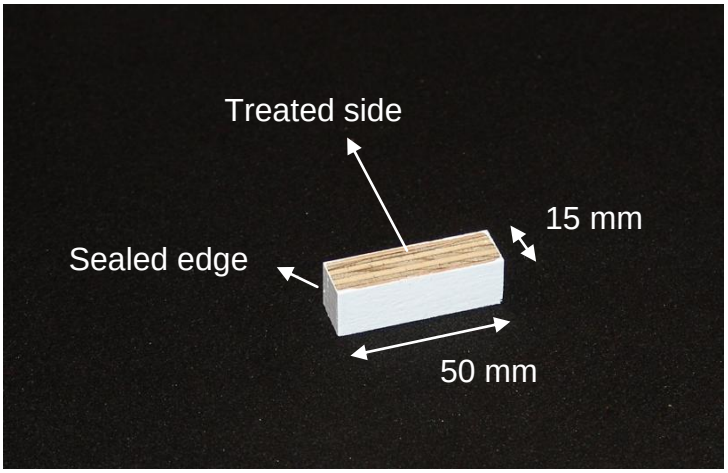

Figure 8.1: Picture of an edge experiment specimen

After being conditioned at 20 °C and 65 % RH, one of the two unsealed edges of each block was brushed twice with one of the pure products W2, W3 or W5. Consequently the specimens were subjected to an imbibition experiment simulating the water absorption caused by wind-driven rain on the façade or exterior cladding of a building envelope (Mukhopadhyaya et al. 2002). Therefore the specimens were put with their treated edge onto a stainless steel grid in contact with a shallow layer of demineralised water, this way avoiding internal pressure (Lukowsky et al. 1998; Candanedo and Derome 2005). The mass and width of each specimen was determined prior to the water contact and after 5 s, 5, 10 min, 1, 2 and 4 h. The specimens were also removed from the water after 4 hours sorption and allowed to dry under constant temperature (20 °C) and humidity conditions (65 % RH). They were reweighed and measured after 1, 20 and 44 h desorption. All these values were then used to calculate the MC (Chapter 7, Eq. 7.7), the water repellent effectiveness WRE (Chapter 7, Eq. 7.6) and the swelling in the middle of each specimen (Eq. 8.1) at the different times t.

$$swelling\ (\%) = \frac{width_t\ (mm) - width_{t_0}\ (mm)}{width_{t_0}(mm)} \tag{8.1}$$

During sorption water penetrates the wood block by different forms of diffusion and capillary forces (de Meijer and Militz 2000; Mukhopadhyaya et al. 2002). The waterfront moves up in the block and finally reaches the opposite side. From now on the wood block is capillary saturated and moisture absorption is the result of diffusion and dissolution and removal of air inclusions in the water (Mukhopadhyaya et al. 2002; Roels et al. 2004; Hens 2007). These two phases can clearly be distinguished from each other when the water inflow per square meter of contact surface is plotted versus the square root of time. Both phases have a linear relationship being typical for hygroscopic porous materials, but with a distinctly different slope (Krus et al. 1997). The intersection defines the capillary saturated volumetric moisture content w_c (kg/m^3) and is a net material property. The slope of the curve in the first phase is called the water absorption coefficient A_w [kg/(m² s$^{1/2}$)] and is a composite property indicating how easily a

material absorbs water. When in direct contact with liquid water, this water absorption coefficient determines, together with the moisture-liquid diffusivity D_w (m^2/s), the moisture transport and the redistribution of the moisture into the wood (Mukhopadhyaya et al. 2002). When assuming constant diffusivity and taking the shape of the advancing moisture front into consideration these two parameters can be linked to each other according to equation 8.2 (Kumaran 1999; Mukhopadhyaya et al. 2002; Candanedo and Derome 2005). Although liquid diffusivity D_w is assumed to be constant, Mukhopadhyaya et al. (2002) proved that D_w of untreated eastern white pine increased with increasing temperature. Bearing equation 8.2 in mind this also has consequences for the water absorption coefficient. That is why this test set-up was performed under constant climatic conditions (20 °C and 65 % RH). Since A_w might be influenced by the superficial treatment with organosilicons it was calculated and this according to equation 8.3 (Kumaran 1999; Candanedo and Derome 2005).

$$D_w(m^2/s) = \frac{\pi}{4}\left[\frac{A_w\,(kg/(m^2 s^{1/2}))}{w_c\,(kg/m^3)}\right]^2 \tag{8.2}$$

$$A_w\left(kg/(m^2 s^{1/2})\right) = \frac{m_{time}\,(kg) - m_{initial}\,(kg)}{contact_{area} \times \sqrt{time}\,(m^2\, s^{1/2})} \tag{8.3}$$

8.3 Results

Floating test – envelope experiment

In the first part of this research no evidence was found that organosilicons applied at low concentrations lead to lower water sorption (both liquid and water vapour) of wood (Chapter 7). Therefore a second line of thinking was developed. Higher concentrations of organosilicons were applied, but since De Vetter et al. (2009b) already indicated that these concentrations were no longer economically feasible for full wood matrix treatment, the application was limited to the envelope or the edges of the material. The product retentions for Scots pine sapwood are given in Table 8.1.

Table 8.1: Product retention (g/m^2) of Scots pine sapwood pre-conditioned under different circumstances and brushed twice with seven undiluted organosilicons

Organosilicon	20 °C, 65 % RH	fibre saturated
W2	148 ± 33	164 ± 51
W3	215 ± 54	131 ± 38
W4	136 ± 43	115 ± 41
W5	167 ± 17	155 ± 16
W6	-	145 ± 21
S1	179 ± 16	147 ± 32
S2	158 ± 4	141 ± 34

For the envelope treatment, firstly Scots pine sapwood was brushed twice with six organosilicons and subjected to a floating test. The same experiment was repeated after weathering during one week (144 h) in an ATLAS UVCON. Figure 8.2 shows that prior to weathering all organosilicons were able to lower the MC of the wood significantly, while this was only valid for certain treatments after weathering. Nevertheless the potential of the treatments was proven and therefore the experiment was continued.

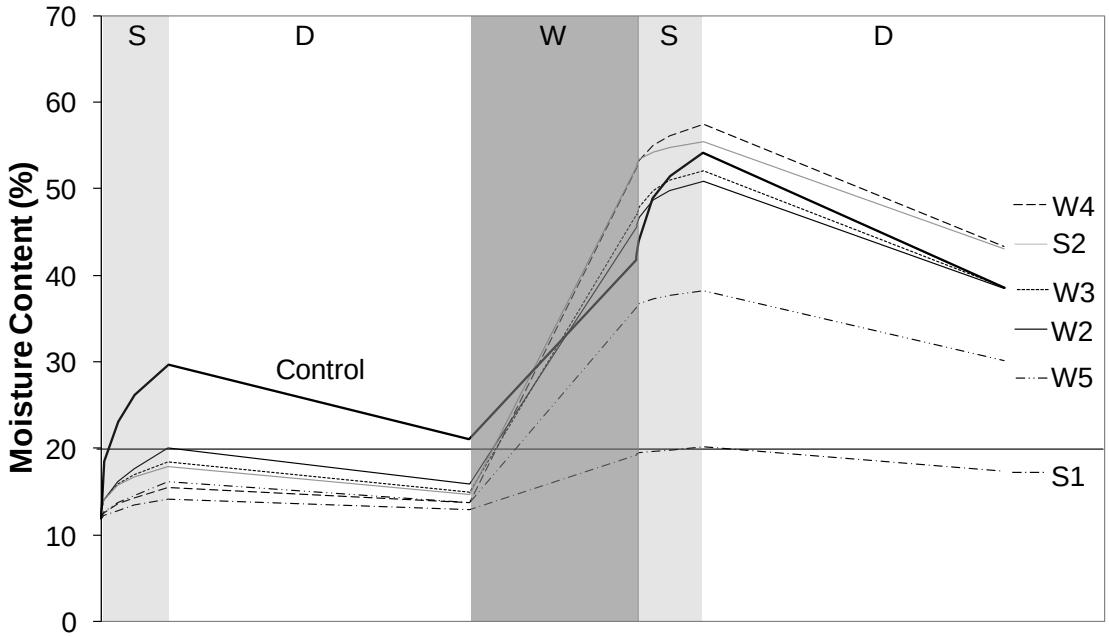

Figure 8.2: Moisture content during sorption (S) and desorption (D) prior to and after artificial weathering (W) of organosilicon treated Scots pine sapwood preconditioned at at 20 °C and 65 % RH

In a next experiment the pure products were applied onto fibre saturated wood, while in the first test the specimens were conditioned at 20 °C and 65 % RH. Figure 8.3 shows the resulting MC over five floating tests, while prior to and in between each floating test artificial weathering was performed. The figure shows that water has accumulated in the wood during this process of weathering and floating, consisting of 4 h sorption and 19 h desorption. Just like in the first floating test prior to weathering all products show their ability to lower the MC of the wood, and this with 40 to 60 %. Afterwards half of the products are losing their effectiveness and the MC is steadily approaching that of untreated Scots pine sapwood. The other products continue to lower the MC with 30 to 70 % and this even after more than 691 hours of alternating floating and weathering. The solvent-based products S1 and S2 perform the best, followed by the emulsions W4 and W5.

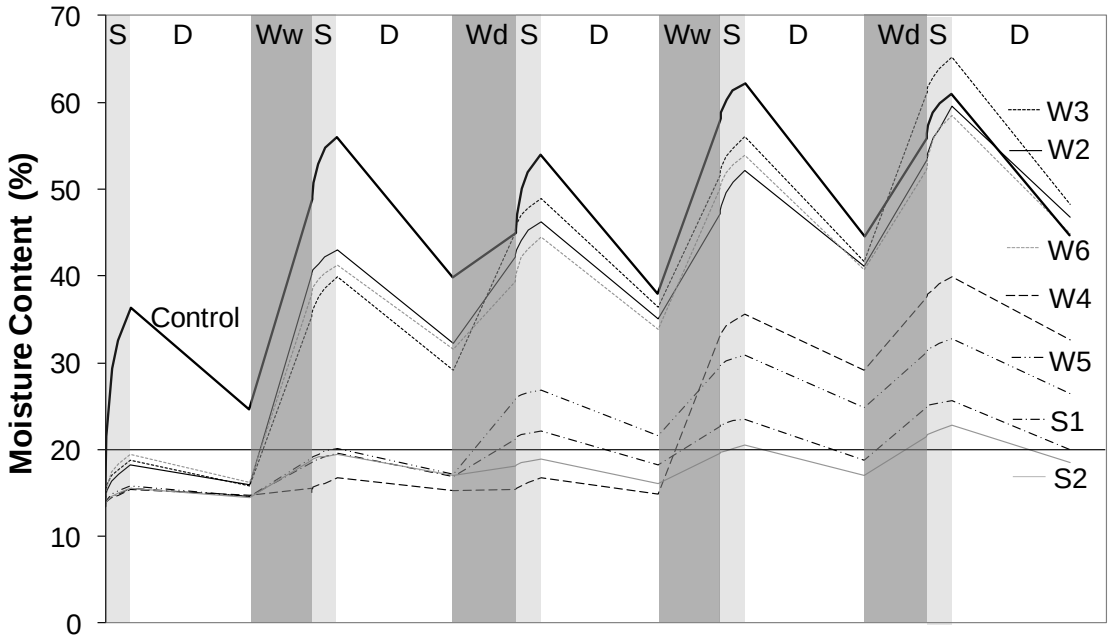

Figure 8.3: Moisture content during sorption (S), desorption (D) and artificial weathering (W) of organosilicon treated Scots pine sapwood pre-conditioned at fibre saturation point. Weathering consisted of alternating a wetter (Ww) and dryer cycle (Wd)

Due to the promising results obtained for protecting solid wood, some organosilicons were applied onto the envelope of plywood and OSB. In Figures

8.4 and 8.5 the course of the MC during floating prior to and after one cycle of artificial weathering of untreated and organosilicon treated plywood and OSB is illustrated. The plywood specimens were brushed twice with product W2, while OSB was treated with either W2 or W4. Figure 8.4 shows that for OSB only slight improvements (15-30 %) can be observed, while for plywood (Figure 8.5) even lower impacts must be noted (<20 %). It must however be stressed that for Scots pine sapwood better results were obtained with other organosilicons, indicating better performance might also be achieved on plywood and OSB when these other organosilicons would have been applied.

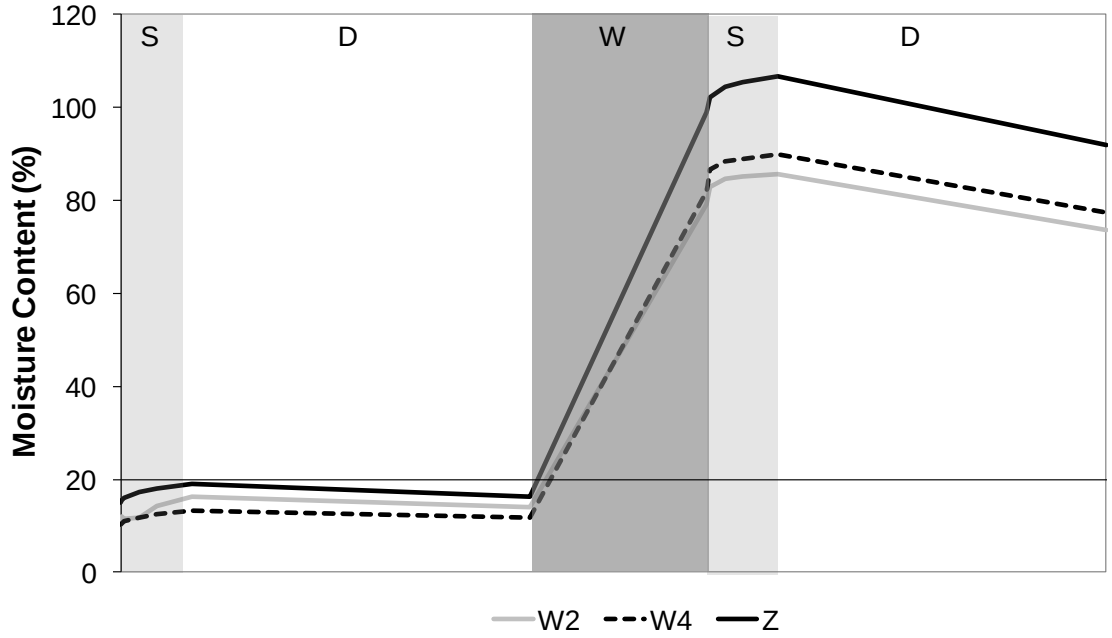

Figure 8.4: Moisture content of untreated and with organosilicon W2 or W4 treated OSB during 4 hours sorption (S) and 19 hours desorption (D) prior to and after 144 h artificial weathering (W)

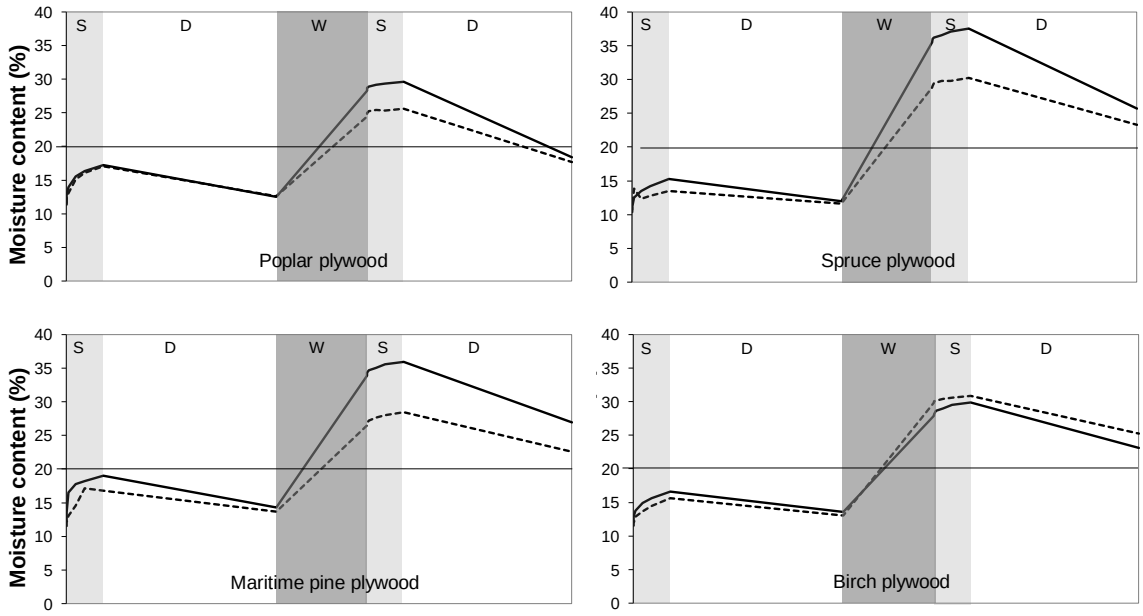

Figure 8.5: Moisture content of untreated (continuous line) and with organosilicon W2 treated plywood (dashed line) 4h sorption (S) and 19h desorption (D) prior to and after 144h artificial weathering (W)

Imbibition test – concentrated edge experiment

Following the superficial application of organosilicons at high concentrations onto wood and wood-based materials, a concentrated edge experiment was set up. Table 8.2 gives the obtained product retentions and shows that for Scots pine sapwood this retention does not differ greatly among the organosilicons, while it does for poplar and birch plywood. These differences are however small compared to the large organosilicon dependent product retentions noted for the re-engineered materials OSB and especially MDF.

Table 8.2: Product retention (g/m^2) of wood-based materials brushed twice with the undiluted organosilicons W2, W3 or W5

Wood-based material	W2	W3	W5
Scots pine sapwood	172 ± 23	184 ± 31	134 ± 15
OSB	295 ± 40	549 ± 60	589 ± 111
MDF	298 ± 25	705 ± 52	1368 ± 149
Poplar plywood	352 ± 67	630 ± 62	547 ± 90
Spruce plywood	315 ± 53	345 ± 63	296 ± 92
Maritime pine plywood	209 ± 23	238 ± 45	213 ± 24
Birch plywood	229 ± 54	401 ± 51	329 ± 35

Figures 8.6 and 8.7 show the moisture contents and swelling of (un)treated Scots pine sapwood, OSB and MDF. They reveal a reduction of moisture content and swelling during sorption and desorption for organosilicon treated Scots pine sapwood, while increased moisture content and swelling is seen for organosilicon treated OSB and MDF compared to their untreated counterparts. Although a fast reduction in moisture content is seen once the specimens were removed from the water, the swelling of most specimens continued for at least another hour.

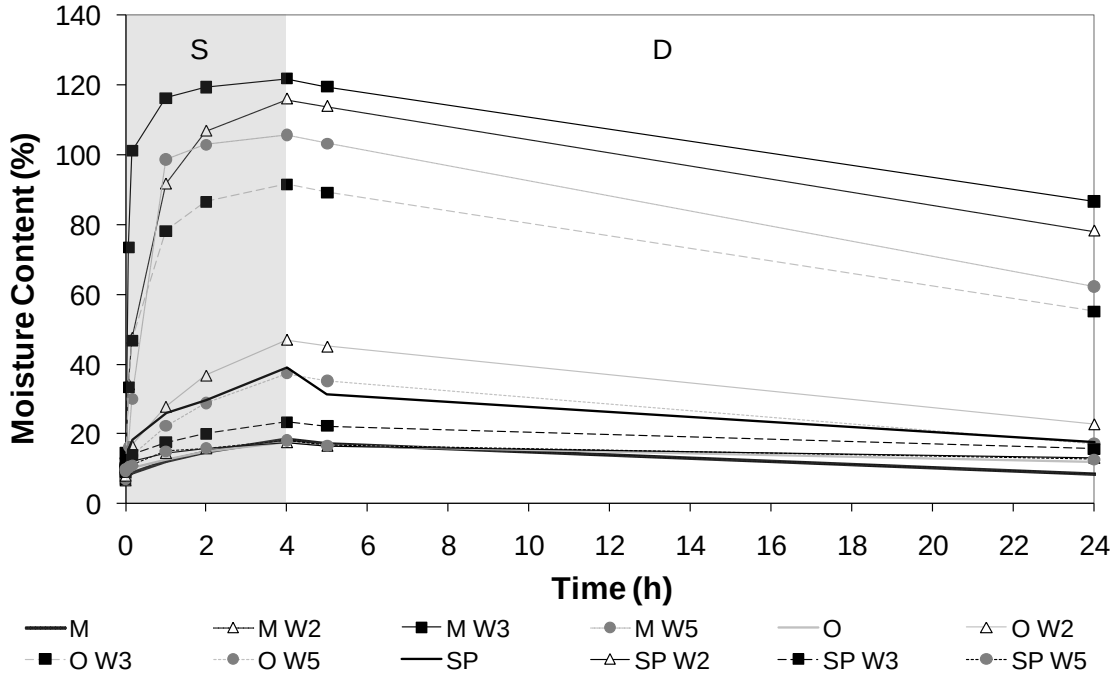

Figure 8.6: Moisture content during sorption (S) and desorption (D) of edges of MDF (M), OSB (O) and Scots pine sapwood (SP), either left untreated or brushed with organosilicons W2, W3 or W5

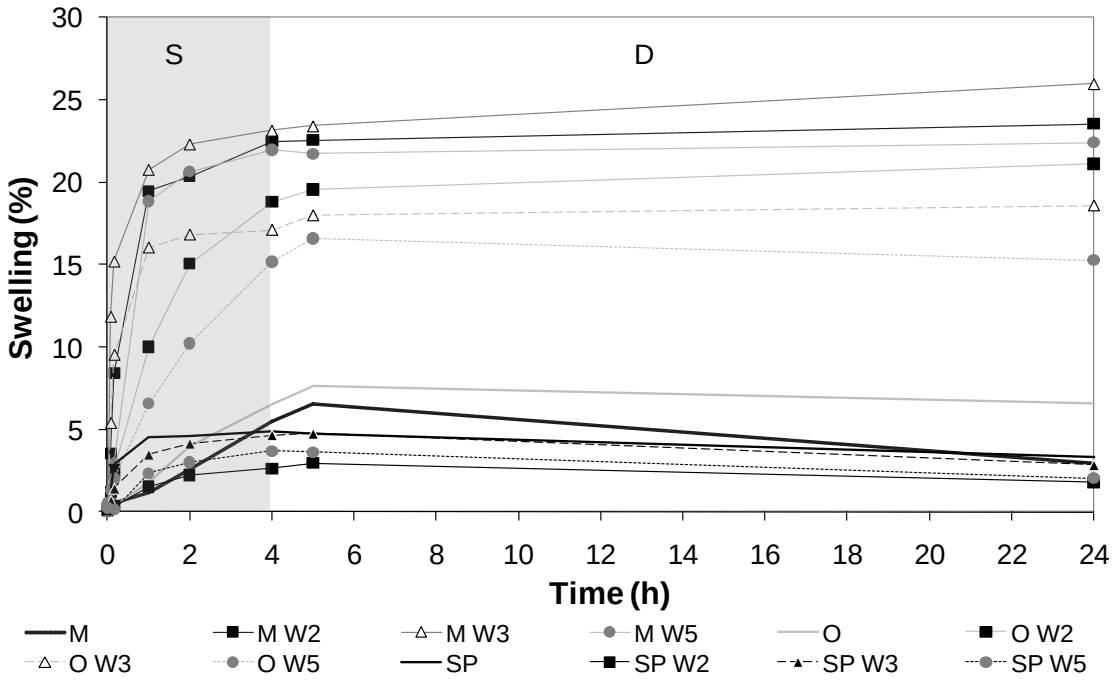

Figure 8.7: Edge swelling of MDF (M), OSB (O) and Scots pine sapwood (SP) specimens during sorption (S) and desorption (D). The specimens were either left untreated or brushed with the organosilicons W2, W3 or W5

For plywood the graphs are not so univocal (Figures 8.8 and 8.9). While the MC is lowered by application of all organosilicons, the swelling is only reduced when W3 or W5 are applied. Application of W2 leads to swelling which is at least as high as the one of untreated plywood. As expected the WRE for MDF and OSB is negative during this experiment, while WRE values of 50 to 65 % are observed for Scots pine sapwood after 4 hours sorption. For plywood a broad range in WRE-values going from 10 to 70 % is found, depending both on the organosilicon applied and on the kind of plywood (data not presented).

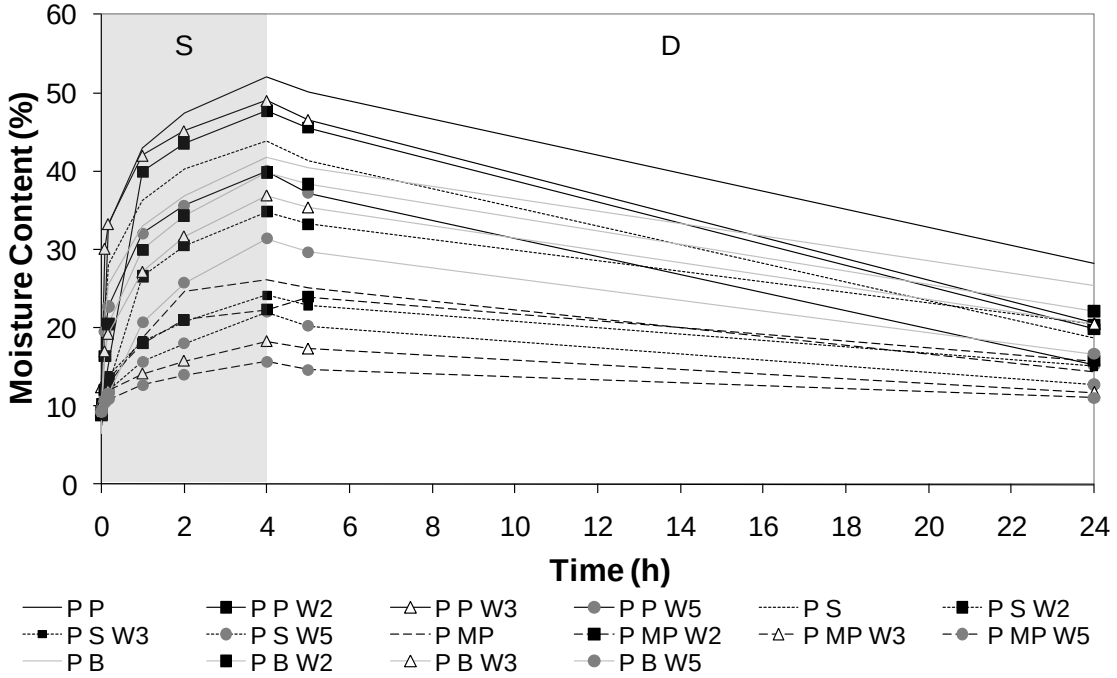

Figure 8.8: Moisture content during sorption (S) and desorption (D) of edges of poplar plywood (P P), spruce plywood (P S), Maritime pine plywood (P MP) and birch plywood (P B). They were either left untreated or treated with organosilicons W2, W3 or W5

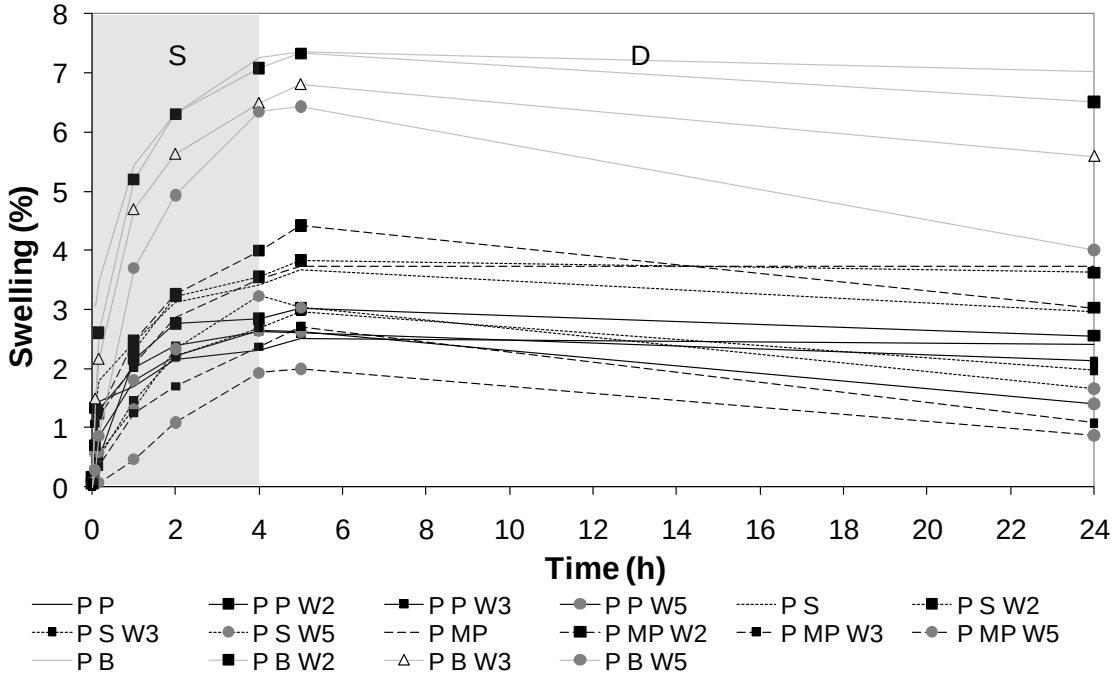

Figure 8.9: Edge swelling of poplar plywood (P P), spruce plywood (P S), maritime pine plywood (P MP) and birch plywood (P B) specimens during sorption (S) and desorption (D). The specimens were either left untreated or brushed with the organosilicons W2, W3 or W5

Table 8.3 shows the resulting water absorption coefficients (A_w) for untreated and organosilicon treated Scots pine sapwood, plywood, OSB and MDF. As could be expected the saturated capillary moisture content (w_c) of Scots pine sapwood was not reached within 4 hours of sorption. This means that the sorption was still in the first phase and all data points of cumulative inflow versus square root of time were used in the linear regression being the basis for the determination of the water absorption capacity. This was also valid for untreated OSB and MDF. The untreated plywoods in contrast reached the saturated capillary moisture content (w_c) already after circa 10 to 115 min, depending on the type of plywood. Therefore a distinction had to be made between the first and second phase of sorption. Visual interpretation of moisture inflow versus square root of time was used to assign each data point to the appropriate phase. Only those points belonging to the first phase were used in the regression analysis leading to the water absorption coefficient.

Table 8.3 shows that all organosilicons lower A_w considerably for solid Scots pine sapwood. This is to a lesser extent the case for all plywoods, except for poplar plywood treated with W3. For the three other types of plywood best performance was achieved with product W5, followed by W3 and W2. Product W5 succeeded for all three plywoods and W3 for maritime pine and spruce plywood in reducing the water absorption coefficient so effectively that w_c is not reached within 4 hours sorption.

The re-engineered materials OSB and MDF in contrast behaved opposite. While their A_w values were the lowest of all untreated specimens, these values increased after application with organosilicons. This increase was so dramatic for OSB treated with W3 and for MDF treated with organosilicons that they reached the saturated capillary moisture content already after circa 10 to 70 min.

Table 8.3: Water absorption coefficient A_w (kg/(m² $s^{1/2}$)) for different wood materials either untreated or brush-treated with organosilicon W2, W3 or W5. Those values given in italics did not reach the saturated capillary moisture content w_c during the experiment

Wood material	Control	Brushed with		
		W2	W3	W5
Scots pine sapwood	*0.02105*	*0.00730*	*0.01158*	*0.00831*
Poplar plywood	0.05334	0.03449	0.06194	*0.03859*
Spruce plywood	0.04366	0.03074	*0.00828*	*0.00717*
Maritime pine plywood	0.01421	0.01300	*0.00505*	*0.00367*
Birch plywood	0.07504	0.05059	0.03802	0.01899
OSB	*0.00586*	*0.02666*	0.12022	*0.01893*
MDF	*0.00912*	0.15242	0.35829	0.16361

8.4 Discussion

In this part of the research preference was given to apply highly concentrated organosilicons onto (part of) the envelope of wood materials. The results of the envelope treatment nevertheless confirm the statements for solid wood: (1) organosilicons are able to lower the moisture uptake of treated wood, (2) but their effectiveness is for most organosilicons reduced a lot by weathering. Extrapolation towards re-engineered materials is however not self-evident. Nofal and Kumaran (1999) have examined the behaviour of OSB in a cyclic wetting and drying experiment. They found that sealing the edges of panels reduced the MC by 5 % and decelerated the board thickness increase. This is important since thickness increase affects the volume of air cavity in the wall and may subsequently affect its functionality.

In the floating test of this study, where the edges were sealed anyway, reduced MC up to 15 % was recorded when the boards were brushed with an organosilicon. However, comparing Figure 8.4 with Figures 8.2 and 8.3 shows that OSB boards in direct contact with water during the floating test have a moisture uptake which is several times the moisture uptake of solid Scots pine

sapwood. In contrast this is not the case when the edges of untreated OSB and MDF are considered and compared to the transverse surface of untreated Scots pine sapwood (Figure 8.6). Although it is already known that the thickness swell of OSB is greater than the swelling of solid wood, and this due to release of compaction stress created during pressing (APA No. TT-028, 1994), this should seen in its proper context. At the beginning of the edge swelling test, Scots pine sapwood swells fast, but also soon reaches its maximum (Figure 8.7). OSB and MDF in contrast have a continuous increase in swelling during the whole sorption period and continue to swell at the beginning of the desorption stage. So initially OSB and MDF are less swollen than Scots pine sapwood, but after approximately 2 and 3.5 hours sorption respectively, this is reversed. Taking the higher moisture uptake and ultimate increased swelling into consideration, it is not surprising that negative WRE values are recorded for OSB and MDF (data not presented).

It has been shown before that the moisture content of wood-based panels exposed to direct wetting is influenced by wetting time and by panel characteristics that affect capillarity such as veneer species of plywood and wax additives of OSB (APA No. TT-028, 1994). Figure 8.5 shows that organosilicon W2 (40 % DMS/n-OTES) succeeds in a slight reduction (<20 %) of the MC of each type of plywood except birch plywood. Focussing on the edges of the boards, reductions of MC between 5 % and 50 % can be achieved, depending on the plywood type and organosilicon applied (Figure 8.8). The order of magnitude of MC and swelling of plywood during the envelope and edge swelling tests are comparable to Scots pine sapwood. In contrast to OSB not all organosilicons succeed in reducing the swell of plywood. Between the different plywood types differences in MC and swelling are seen, caused by panel characteristics like wood species, thickness and number of plies, glue type, etc.

As stated above the water absorption coefficient A_w governs the liquid moisture movement into a material. For wood used in use class 3 conditions, i.e. cladding as part of a building envelope, it is of utmost importance to determine this water

absorption coefficient. This is because it is one of the most important hygrothermal properties necessary to set out the overall moisture management of a building envelope (Mukhopadhyaya et al. 2002). Up to now A_w has been determined for coatings alone or applied onto wood (Hora 1994; Ahola et al. 1999; de Meijer and Militz 2000) and for untreated softwood (Mukhopadhyaya et al. 2002; Candanedo and Derome 2005; Miniotaite 2005) but not yet for wood treated with organosilicons.

Like for longitudinal sawn eastern white pine (Mukhopadhyaya et al. 2002), the second sorption stage was not yet reached for Scots pine sapwood in this edge imbibition test. This means that the moisture content was still below the capillary saturated moisture content. Mukhopadhyaya et al. (2002) found a water absorption coefficient at a water bath temperature of 21 °C of on average 0.0112 kg/(m^2 $s^{1/2}$). Miniotaite (2005) and Kumaran (1999) both reported an A_w value for spruce equal to 0.0096 kg/(m^2 $s^{1/2}$). The water bath temperature was equal to 22 °C in the first report. Candanedo and Derome (2005) found A_w values between 0.00966 and 0.01560 kg/(m^2 $s^{1/2}$) for undefined longitudinal sawn softwood. Logically they found lower values for radial [0.00194 kg/(m^2 $s^{1/2}$)] or tangential [0.00265 – 0.00286 kg/(m^2 $s^{1/2}$)] sawn specimens.

The average A_w value found in this research [0.02105 kg/(m^2 $s^{1/2}$)] for radial/tangential Scots pine sapwood was in the same order of magnitude, but higher than the previously mentioned values. Application of organosilicons lowers this water absorption coefficient 3 to 6 times, but still remains higher than literature values reported for transverse sections of softwood. Ahola et al. (1999) determined water absorption coefficients for coatings on spruce and pine and reported values between circa 0.005 and 0.040 kg/(m^2 $h^{1/2}$), so much lower than the in this research obtained values for organosilicon treated wood. This means coatings are better in reducing the water absorption coefficient of Scots pine than organosilicons. It is suggested that moisture movement through a coating is controlled by diffusion and not by capillarity (Ahola et al. 1999) while

capillary liquid flow is important in uncoated wood after longer exposure times (de Meijer and Militz 2000).

The mode of action of the organosilicons may be parallel to their application onto earth substrates. In that case the silicone can adsorb on the substrate capillaries to form a hydrophobic polysiloxane thin film which can significantly increase the contact angle of water with the substrate capillary wall and reduce the water absorption of the substrate through capillary depression (Noll 1968; Ren and Kagi 1995). Since positive correlations between contact angles of water on coated wood and water absorption rates have been found before, this seems a plausible explanation (Hora 1994; de Meijer and Militz 2000). It was stated before that water repellents, meant to lower the velocity of water uptake and not the maximum water uptake, can cause a reduction of the capillary tension of wood and even a capillary depression (Lukowsky and Peek 1997). De Vetter et al. (2006) found a discontinuous micro-porous network on the cell walls and in the lumens of tracheids and wood rays of Scots pine sapwood after dipping in a low concentrated organosilicon. It can therefore be assumed that highly concentrated organosilicon at the surface could lead to a thin film on the surface, leading to reduced contact angle and lower water absorption coefficient.

While the results for plywood follow the same line as for solid Scots pine, other factors seem to play a role for the re-engineered materials MDF and OSB. After superficial application of organosilicons they absorb more water than their untreated counterparts. Since the matrices of OSB and MDF are significantly different from those of solid wood, and knowing that their sorption behaviour is differently, it could be that organosilicons react in another way with these materials than they do with solid wood. However, the exact reason why both materials absorb more water after superficial treatment with organosilicons is still an open question that needs to be resolved.

8.5 Conclusion

Superficial treatments at high concentrations show potential in improving water repellent characteristics of solid wood and plywood. Drawback is the reduced effectiveness after artificial weathering. Considering the re-engineered materials OSB and MDF, organosilicons behaved opposite as expected. They increased the moisture uptake of the edges and consequently the swelling. The mode of action of this process is not yet known and forms a challenge to the future.

Acknowledgements

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9 PREVENTIVE ACTION OF ORGANOSILICON TREATMENTS AGAINST DISFIGUREMENT OF WOOD UNDER LABORATORY AND OUTDOOR CONDITIONS[1]

Abstract

Organosilicons and biocides with known effectiveness against fungal disfigurement were used for dipping or impregnating Scots pine sapwood specimens. All specimens were artificially or naturally weathered and the colour of all specimens was determined with a spectrophotometer at fixed times. After artificial weathering the specimens were used in blue stain tests according to EN 152 or according to the EN 152 reverse method. The naturally exposed specimens were inspected for fungal disfigurement on their back side. Although the results learn that the coating approach is far better than the wood preservatives approach for evaluating blue stain attack of organosilicon treated wood, organosilicons fail to protect wood under laboratory conditions. Outdoor exposure, however, revealed that organosilicon impregnated specimens were better protected against fungal disfigurement. The addition of a biocide improves the performance. Artificially aged specimens did not show significant colour differences compared to untreated Scots pine sapwood, while naturally aged specimens did, depending on the treatment conditions and presence of biocides. Organosilicons are able to reduce leaching of (degraded) wood constituents, leading to fewer colour changes compared to untreated Scots pine and to decreased availability of nutrients for superficial fungal growth.

[1] Accepted as:
De Vetter, L., Van den Bulcke, J., De Windt, I., Stevens, M., Van Acker, J,. accepted. Preventive action of organosilicon treatments against disfigurement of wood under laboratory and outdoor conditions. International Biodeterioration and Biodegradation.

9.1 Introduction

Wood is a building material that, due to its diversity, can be applied in a broad range of applications. Depending on the type of application specific demands of the wood are required ranging from architectural or technical specifications to customer-driven demands. For most customers appearance is the decisive factor in their choice between wood and synthetic, metal or mineral alternatives in favour of wood. Measuring customer preferences is however not straightforward. For outdoor wood applications fungal disfigurement and colour are two main factors determining the appearance (Salča and Fotin 2007).

Organosilicons have proven effectiveness as hydrophobing agents in for example the textile, paper and building industry (Rochow 1987; Hager 1995; Lukowsky and Peek 1997; Roos et al. 2008). Their suitability to protect wood was suggested and aspects like durability, moisture stability etc. have been investigated (Hager 1995; Tshabalala et al. 2003; Mai and Militz 2004b; De Vetter and Van Acker 2005). However, most studies found that treatment of wood with organosilicons can only lead to a significant improvement of the investigated property when applied at (very) high concentrations (Hill et al. 2004; Weigenand et al. 2007; De Vetter et al. 2009b). Treatments at lower, economically feasible concentrations lead to only modest improvements of the wood properties (Goethals and Stevens 1994: Mai et al. 2005; De Vetter et al. 2009a). Nevertheless, most of these authors conclude that wood treatment with an organosilicon may contribute significantly to prolong the service life of the wooden element when applied as part of a more complex (preservative containing) formulation for use class 3 applications like exterior cladding (Mai et al. 2005; Donath et al. 2006; De Vetter et al 2009a, 2009b).

It was therefore the purpose of this study to evaluate both fungal disfigurement and colour change of organosilicon treated wood under use class 3 applications (EN 335-1 2006). Therefore a broad range of different organosilicons was used as test group. For a subgroup of specimens organosilicons were combined with biocides. Depending on the test set-up they were applied using dipping or vacuum impregnation. Both laboratory and outdoor field tests were performed

investigating the performance of the applied systems under the specific circumstances.

9.2 Materials and methods

9.2.1 Products

Both organosilicon solutions as such, as well as combinations of an organosilicon with a biocide were used to treat the specimens. The organosilicons cover both solvent-based and water-based systems (De Vetter et al. 2009a, 2009b). Basically two 100 Wt % active solvent-based alkoxysilanes were tested. The first product S1 contained only N-octyltriethoxysilane (n-OTES) and the second S2 was a combination of n-OTES and methyltrimethoxysilane (MTM). Furthermore a 50 % Wt active emulsion of methoxy-terminated dimethylphenylsiloxane (DMS) and n-OTES (DMS/n-OTES 1) called W1 and a 100 % Wt active micro-emulsion of polydimethylsiloxane (PDMS) and triethoxysilane (TES) referred to as W4 were included. Finally also a 40 % Wt active mixture of DMS and n-OTES (DMS/n-OTES 2, W2) and a 60 % Wt active macro-emulsion of PDMS (W3) were used. All these products were developed at the laboratories of Dow Corning Corporation (Belgium), except for the 100 % PDMS/TES which was obtained from Wacker-Chemie GmbH (Germany). The solvent-based and water-based systems were diluted up to 5 Wt % with isopropylalcohol and water, respectively.

The same combinations of organosilicons and biocides as used in De Vetter et al. (2009a) were applied. Briefly, a 5 % solution of the 40 % DMS/n-OTES (W2) was combined with (1) 0.3 % 3-iodo-2-propynyl-butyl carbamate (IPBC, B1); (2) 0.3 % IPBC in combination with 0.6 % (±)-(cis+trans)-1-(2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl-methyl)-1H-1,2,4-triazole (propiconazole, B3) and (3) 2 % 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride (Si-Quat, B2). As a solvent-based counterpart 5 % Wt MTM/n-OTES (S2) was combined

with (1) 0.3 % IPBC and (2) 0.3 % IPBC in combination with 0.6 % propiconazole. Thirdly 10 % MTM/n-OTES was combined with 1 % Si-Quat. Summarizing six organosilicons and six combinations of an organosilicon and a biocide were applied. In addition to the treated specimens, untreated Scots pine sapwood (Z) reference specimens were included in the tests as well. Moreover, in the natural weathering test untreated heartwood of Scots pine (Gk), Douglas fir (*Pseudotsuga* spp., Do) and larch (*Larix deciduas*, La), having the same dimensions as the Scots pine specimens, were added to the pine sapwood references.

9.2.2 Laboratory experiments

Both fungal disfigurement and colour change were evaluated on laboratory and semi-industrial scale. Therefore pre-conditioned (12 % moisture content) straight grained Scots pine (*Pinus sylvestris* L.) sapwood was used. For the laboratory experiments the wood was sawn to 320 × 40 × 10 mm (L × R × T) and the end-grain cross sections were sealed twice with a 2-component water impermeable polyurethane system. The specimens were subsequently dipped for a few seconds into the treating solutions into four replicates. They were weighed before and after dipping, allowing calculation of the product and active ingredient retention of organosilicon and biocide (Chapter 1, Eq. 1.4 and 1.5). The specimens were placed into an Atlas UV2000 and artificially weathered during six weeks using a test cycle as described in the new draft version of EN 152. Prior to weathering and in between two subsequent cycles, consisting of a wetter and dryer subcycle, the colour was determined (see further).

Afterwards the specimens were conditioned at 20 °C and 65 % RH. Out of every weathered specimen four smaller specimens were sawn for blue stain evaluation. Two had the dimensions of standard EN 152 specimens (90 × 40 × 10 mm, 2003, Figure 9.1 a), while two smaller specimens were sawn according to the recommendations for the reverse EN152 method (50 × 40 × 10 mm, Van

den Bulcke et al. 2006, Figure 9.1 b). The first method is the so-called wood preservatives approach, while the latter is the wood coating approach.

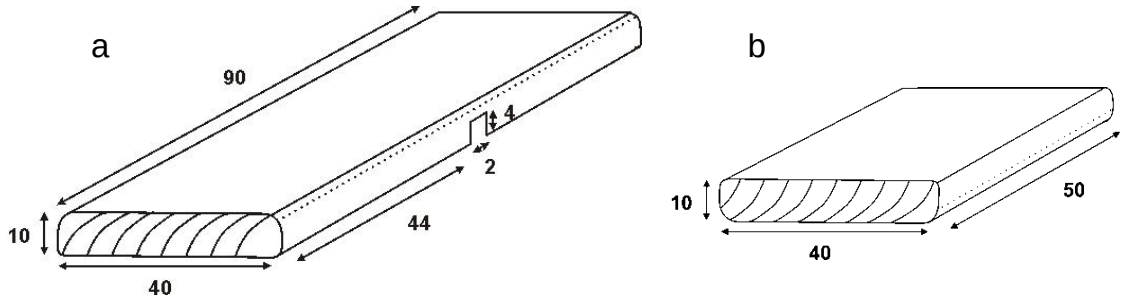

Figure 9.1: Specimen dimensions according to (a) the standard EN 152 test and (b) the EN 152 reverse method

The EN 152 specimens were planed at the non-weathered side removing the applied organosilicon (and biocide) leading to an untreated surface, easy accessible for fungi. In contrast, half of the reverse specimens were sealed on all but the weathered side, forcing the fungi to grow through the weathered organosilicon (and biocide) layer. The other reverse specimens were sealed on all but the non-weathered side, this time preventing fungal growth from any side, except via the non-weathered organosilicon (and biocide) layer. The sealant was a translucent 2-component polyurethane system doped with dichlofluanid to prevent staining. In total eight different standard EN152-specimens, four reverse weathered and four reverse non-weathered specimens per treatment, were each exposed in a single jar to blue stain attack. Besides these treated specimens four artificially weathered as well as non-weathered untreated Scots pine sapwood specimens were included in the test as reference specimens.

A spore suspension of *Aureobasidium pullulans* var. pullulans (de Barry) Arnaud and *Sydowia polyspora* (Bref & Tavel) E. Müll. was prepared as explained in Van den Bulcke et al. (2006). After the specimens were γ-sterilised (1.5 Mrad), they were shortly dipped in the spore suspension and put on a vermiculite substrate after which another 15 ml of spore suspension was poured over the specimens. After six weeks incubation at 22 °C and 70 % RH a visual, exterior assessment of the blue stain specimens, excluding the edges, was

performed according to the rating scale as defined in EN 152, namely: 0: not blue stained; 1: insignificantly blue stained; 2: blue stained; 3: strongly blue stained. These classes were further subdivided using 0.5 increments, as proposed by Van den Bulcke et al. (2006) to have more precise ratings. For the interior assessment the EN 152 specimens were cut parallel to the end faces at 30 mm from each end (EN 152), while the reverse specimens were sawn in half. The rating scale as proposed by Van Acker et al. (1998) was used for the evaluation with: 0: no blue stain found; 1: few spots of blue stain; 2: small blue stained areas; 3: specimen is partly blue stained, but there are still areas free of blue stain; 4: the major part of the specimen is blue stained; 5: cross-cut of the specimen is completely blue stained.

9.2.3 Outdoor performance testing

For the semi-industrial scale or outdoor experiments Scots pine sapwood specimens of 375 × 100 × 20 mm (L × R × T) were used, which were also sealed at both end-grain cross sections in the same manner as for the laboratory scale tests. Half of these specimens were dipped into the treating solutions, while the other half was vacuum impregnated in the same solution using a pressure of 5 bars for 45 minutes. After releasing the pressure the specimens stayed submerged for another 15 minutes at atmospheric pressure. They were finally removed from the tank and allowed to drip for 15 minutes. Four replicates per treating solution and treatment procedure were used. Mass of each specimen was measured prior to and after treatment allowing calculation of the organosilicon (and biocide) product retention (Chapter 1, Eq. 1.2) as well as weight percent gain (WPG, Eq. 1.1) for the impregnated specimens. The treated specimens were then dried at 60 °C until they reached constant mass.

After conditioning at 20 °C and 65 % RH the specimens were weighed again, inspected visually and mounted outdoors on a rack having an inclination of 45° and facing south-southwest (EN 927-3 1996). The rack was located at the

outdoor weathering site of the Laboratory of Wood Technology (Ghent University) in Ghent, Belgium. The specimens were not inoculated with any spore suspension.

Donath (2004) already demonstrated that visually evaluating the back, and thus non-weathered side (facing north) of such outdoor exposure specimens reflects well the resistance against moulds of a product. Therefore, for the evaluation of fungal disfigurement the specimens were visited every season and evaluated externally on their back for fungal disfigurement. Although most fungi were moulds, other fungi were not disregarded. The following rating scale was drawn up and used to classify each specimen: 0: no fungal disfigurement; 1: small spots of fungi are detected; 2: fungi in a small band at the upper part of the specimen; 3: fungi scattered in broader bands over the surface of the specimen; 4: specimen' surface completely overgrown with fungi.

For the colour evaluation the specimens were removed from the rack and conditioned for seven days at 20 °C and 65 % RH every year. Afterwards the colour was measured at the front side, facing south-south west.

9.2.4 Colour evaluation

For the colour evaluation a Spectrophotometer Konica Minolta CM-2600d was used and the obtained colour was expressed as a CIE*Lab-value. Per specimen five colour measurements were performed, which were averaged to a mean value of L*, a* and b*. L* represents the lightness of the specimen and ranges from black (0 %) to white (100 %), while a* and b* are chromaticity values representing the red to green and yellow to blue colour, respectively. It is plausible to assume that for a customer once he has chosen for a certain wood product, not the colour as such but the colour change over time is of major importance in the appreciation of the wood product. Therefore preference was given to evaluate the colour difference ΔE of each specimen and this considering both the application of a treatment product as well as the time of

weathering. Therefore ΔE was calculated as the colour difference between each specimen at a certain time t compared to the colour of untreated and non-weathered Scots pine sapwood (Eq. 9.1). The reference values for L*, a* and b* were the average values of all untreated and non-weathered Scots pine sapwood specimens included in the artificial weathering test.

$$\Delta E = \sqrt{\left(L_t^* - L_{ref}^*\right)^2 + \left(b_t^* - b_{ref}^*\right)^2 + \left(a_t^* - a_{ref}^*\right)^2} \quad (9.1)$$

9.2.5 Statistics

Since for fungal disfigurement only a limited number of replicates were used and the rating is nonlinear anyhow the median value was preferred over the average value as to minimise the impact of outliers. Furthermore it is not the purpose to evaluate products but to retrieve information whether organosilicons as a group can decrease fungal disfigurement. Therefore the obtained rating values were not interpreted as such, but used to make clusters of products performing the same as, better than or much better than untreated Scots pine sapwood. To lower the impact of outliers the Partitioning Around Mediods (PAM) cluster analysis was preferred. The analysis was performed for each testing protocol separately (EN152, reverse weathered and reverse non-weathered) and for combinations of tests. The number of clusters to retain was determined using scree analyses. Prior to acceptance of each clustering it was checked whether they could explain at least 80 % of the variability between the treatments. The clusters fulfilling this requirement were then compared with each other.

For the colour evaluation of both tests, using artificial or natural weathering, first a two-way analysis of variance (ANOVA) with fixed factors was performed. The dependent variable was the colour difference ΔE of each specimen compared to untreated Scots pine sapwood prior to weathering and the independent variables were treatment and time. If significant interaction between the

independent factors was found, meaning that ΔE depends on the combination of treatment and time, the two-way ANOVA could not be further interpreted. Therefore a one-way ANOVA was performed with ΔE as dependent variable and a new factor Group as independent variable. Group contains all possible combinations of treatment and time. Consecutive post-hoc analyses using Scheffé-tests revealed which groups differed significantly from each other.

9.3 Results

9.3.1 Product retention

Table 9.1 gives a schematic overview of the product codes, product retentions, active ingredient retentions and WPGs for the different test set-ups.

Table 9.1: Overview of product codes, product retentions, active ingredients and weight percent gains (WPGs) obtained due to dipping (D) or impregnation (I)

Product code	Bluestain test: D		Outdoor test: D		Outdoor test: I	
	Product retention (g/m^2)	Active ingr ret (g/m^2)	Product retention (g/m^2)	Active ingr ret (g/m^2)	Product retention (kg/m^3)	WPG (%)
W1	7.8	3.9	13.3	6.6	59.6	6.0
W2	6.8	2.7	14.6	5.9	91.0	7.4
W3	3.3	2.0	8.9	5.3	52.4	6.3
W4	2.7	2.7	6.0	6.0	32.1	6.4
S1	2.3	2.3	5.1	5.1	27.5	5.6
S2	2.3	2.3	5.7	5.7	29.3	5.9
W2	26.4	10.5	13.6	5.5	54.2	4.5
+ B1	3.7	0.6	1.9	0.3	7.7	0.3
W2	6.8	2.7	18.9	7.6	49.0	4.1
+ B2	1.5	1.1	4.2	3.0	10.9	1.6
W2	9.8	3.9	18.3	7.3	54.3	4.3
+ B3	4.7	0.7	8.8	1.3	26.0	0.8
S2	2.0	2.0	6.3	6.3	14.0	2.9
+ B1	0.7	0.1	2.2	2.2	4.9	0.2
S2	6.3	6.2	8.8	8.8	28.6	5.7
+ B2	0.9	0.6	1.2	1.2	4.0	0.6
S2	2.3	2.3	3.3	3.3	16.3	3.6
+ B3	2.8	0.4	4.0	4.0	19.5	0.6

9.3.2 Laboratory experiments

Fungal evaluation

Clustering the EN 152 data was not possible for the exterior evaluation data and was not satisfactory for the interior EN 152 evaluation data. Nearly all specimens were completely blue stained and had therefore the same exterior rating (Figure 9.2), while less than 80 % of the variability of the interior evaluation could be explained by the treatment (Figure 9.4). Although slight differences in discolouration were observed, they could not be extracted from the analysis. Furthermore the biocides used have proven anti blue stain effectiveness (Isquith et a. 1972) at the concentrations applied (Valcke 1989). Therefore it seems that the wood preservatives approach is not fully suitable for evaluating organosilicon treated wood.

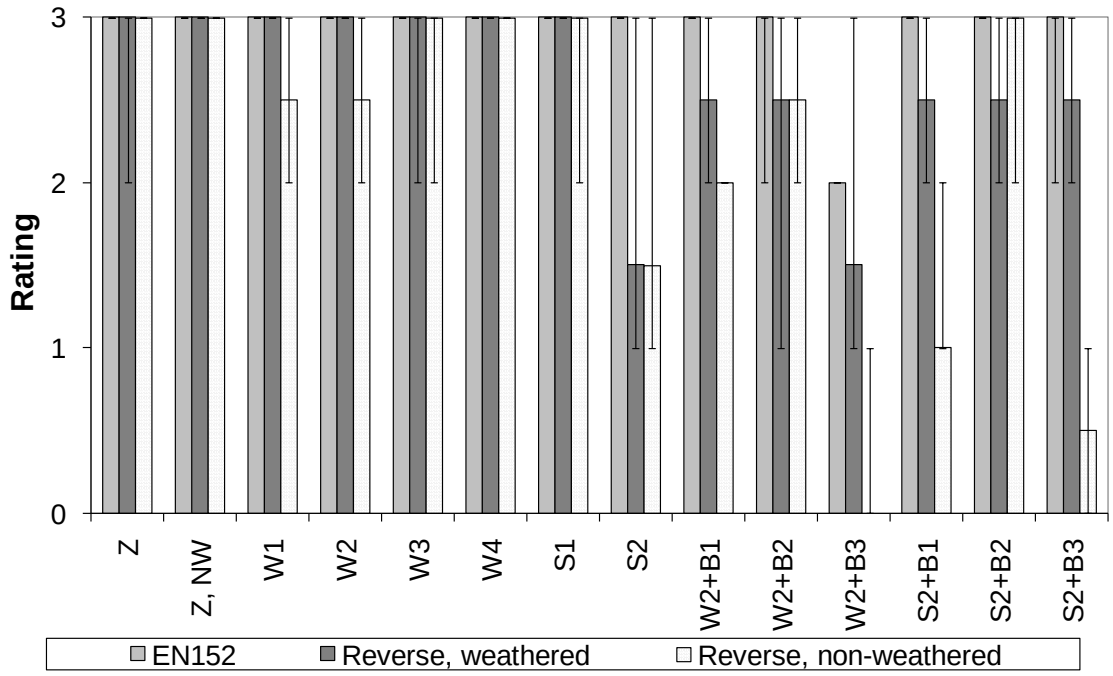

Figure 9.2: Median, minimum and maximum exterior rating of untreated (Z) and organosilicon (W1 to S2) and biocide (B1 to B3) dipped Scots pine sapwood specimens blue stained according to the standard EN 152 method or according to the EN 152 reverse method, weathered or not (NW)

Indeed, the coating approach as defined by Van den Bulcke (2006) is more appropriate for evaluating the blue stain resistance of organosilicon treated

wood. For all reverse data, whether evaluated externally or internal, weathered or not, three clusters were obtained. Untreated Scots pine sapwood and most treatments comprising only an organosilicon belong to the same cluster, the one of worst performing treatments. The cluster with the best performing treatments contains those treatments where IPBC with propiconazole is involved. The other biocide containing treatments most often belong to the intermediate cluster. However, in case of interior evaluation these treatments might also belong to the best performing cluster.

Colour evaluation

The average L*, a* and b* values of untreated and non-weathered Scots pine sapwood specimens were 82.7, 4.6 and 24.3 respectively. They were used both in the artificial and natural weathering tests to calculate the colour difference ΔE. For ΔE significant interaction ($p=0.0$ for both artificially and naturally weathered wood) between treatment and time was found. The consecutive one-way ANOVA revealed significant differences between the groups (both $p=0.0$), leading to Scheffé-tests to discover which groups differ significantly from each other. The mean colour difference ΔE and the corresponding standard deviation are presented in function of the treatment in Figure 9.3 for artificially weathered wood. The figure shows that dipping of untreated Scots pine sapwood in solutions containing DMS/n-OTES 1 (W1) or MTM/n-OTES + Si-Quat (S2 + B2) induce a significant colour difference compared to untreated Scots pine sapwood. The other treatments do not lead to a significant colour difference. Furthermore the figure shows that, as expected, colour difference of untreated Scots pine sapwood increases with time. However, there is no significant colour difference between specimens exposed for the same time period. After the third weathering cycle ΔE increases again, leading to significant colour differences compared to the previous cycle (cycle 2). It can therefore be summarized that among specimens exposed for the same exposure period no major colour differences are present. After one weathering cycle only a small number of treatments have a significantly different ΔE compared to the non-weathered

wood, whereas this number increases after two cycles and is valid for all treatments after three cycles.

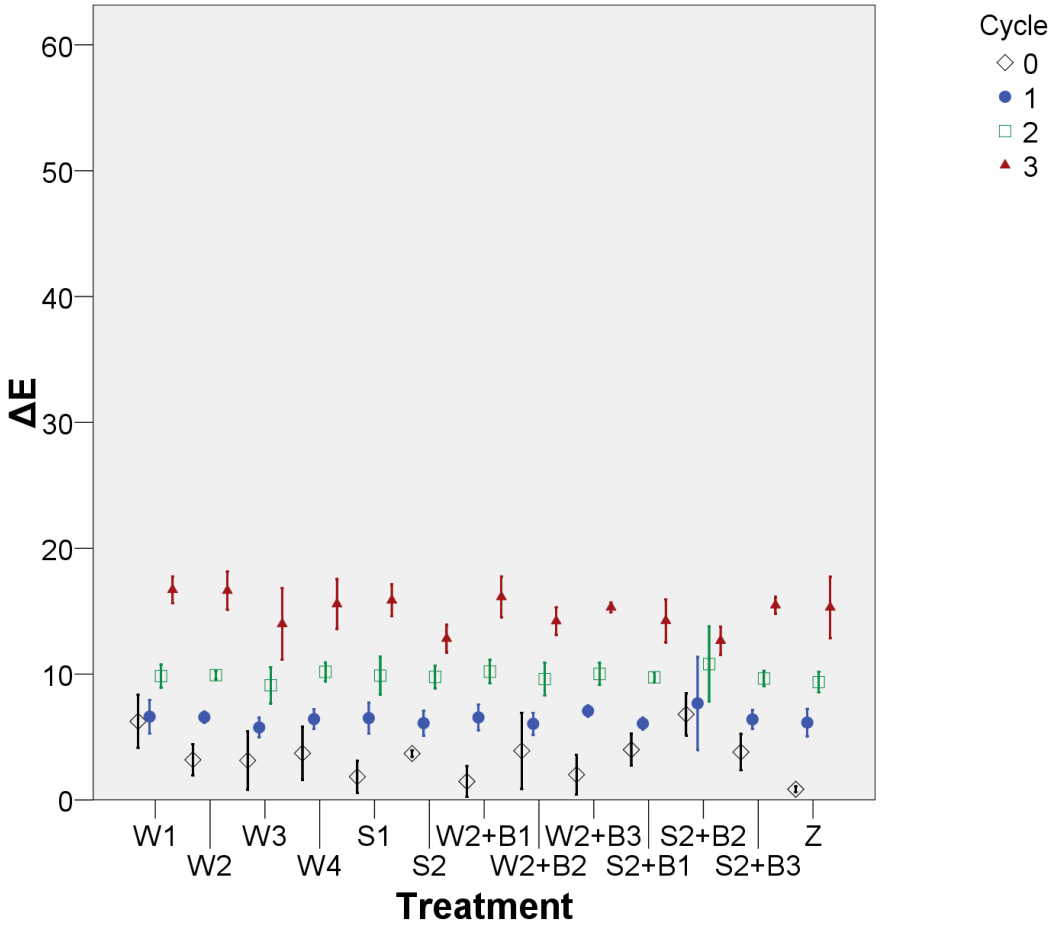

Figure 9.3: Averages and 95 % confidence intervals of the colour change ΔE for untreated Scots pine sapwood (Z) and Scots pine sapwood dipped into an organosilicon (W1 to S2) or into a combination of organosilicons W2 or S2 combined with biocides B1, B2 or B3 (Table 1.1) and this prior to (0) and after 1, 2 and 3 consecutive artificial weathering cycles.

Although the total colour difference is of major importance to consumers, ΔE does not indicate the direction of colour change. Therefore, the components L*, a* and b* were examined in detail (data not presented). None of these values on its own was significantly different from each other or untreated Scots pine sapwood, indicating treatment did not influence the colour parameters. The weathering procedure itself however did influence the colour change, making all specimens discolour in the same manner. The specimens became brighter and

less red until the second weathering cycle after which they became darker and redder, while yellowing continued. Summarizing it can be said that dipping of Scots pine sapwood into an organosilicon solution does not have a significant effect on any of the colour components, while artificial weathering does have a significant effect on the colour.

9.3.3 Outdoor performance testing

Fungal evaluation

Also for the natural weathering test clustering into three groups was the best option (Figure 9.4). Regardless the exposure period untreated Scots pine sapwood specimens and half of the specimens dipped in organosilicons are grouped as worst performing. The other half of the in organosilicon dipped treatments, along with impregnations with organosilicons and dipping in solutions containing Si-Quat are clustered in the intermediate performing group. To the best performing group belong, besides all reference wood species, impregnations containing biocides IPBC and IPBC + propiconazole. The remaining treatments not yet mentioned, are impregnations with an organosilicon and the biocide Si-Quat and dipping including IPBC and IPBC + propiconazole. After one year natural weathering they belong to the best group, while they lose effectiveness over time resulting in a shift towards the medium group after two (and three) years weathering.

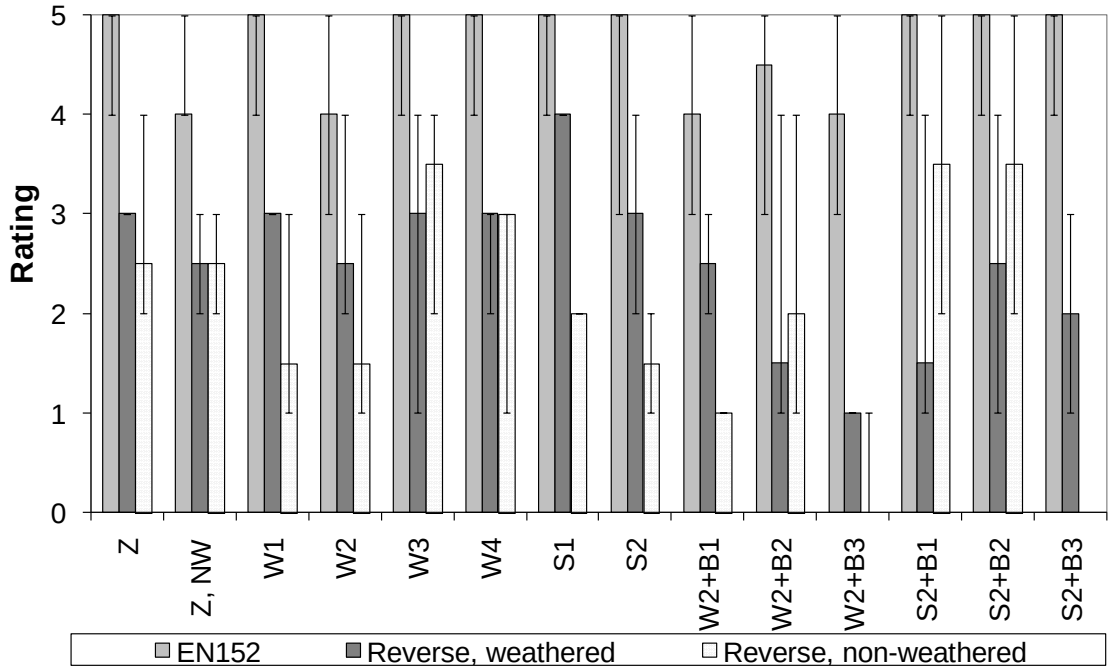

Figure 9.4: Median, minimum and maximum interior rating of untreated (Z) and organosilicon (W1 to S2) and biocide (B1 to B3) dipped Scots pine sapwood specimens blue stained according to the standard EN 152 method or according to the EN 152-reverse method, weathered or not (NW)

Colour evaluation

For the colour evaluation of naturally weathered wood, only Scots pine sapwood was evaluated, whether treated or not. The colour difference ΔE seems far more complicated (Figures 9.5 and 9.6) and doesn't change so uniformly as for artificially weathered specimens. Since the colour data prior to weathering are missing, no conclusions concerning the influence of each treatment on the colour can be made.

The standard deviations of ΔE are much greater than for artificially weathered specimens. Therefore after one year natural weathering there is no significant difference in ΔE value of dipped specimens and untreated Scots pine sapwood, except when the biocides IPBC (B1) or IPBC + propiconazole (B3) are included (Figure 9.5). However, these differences fade away with longer exposure time.

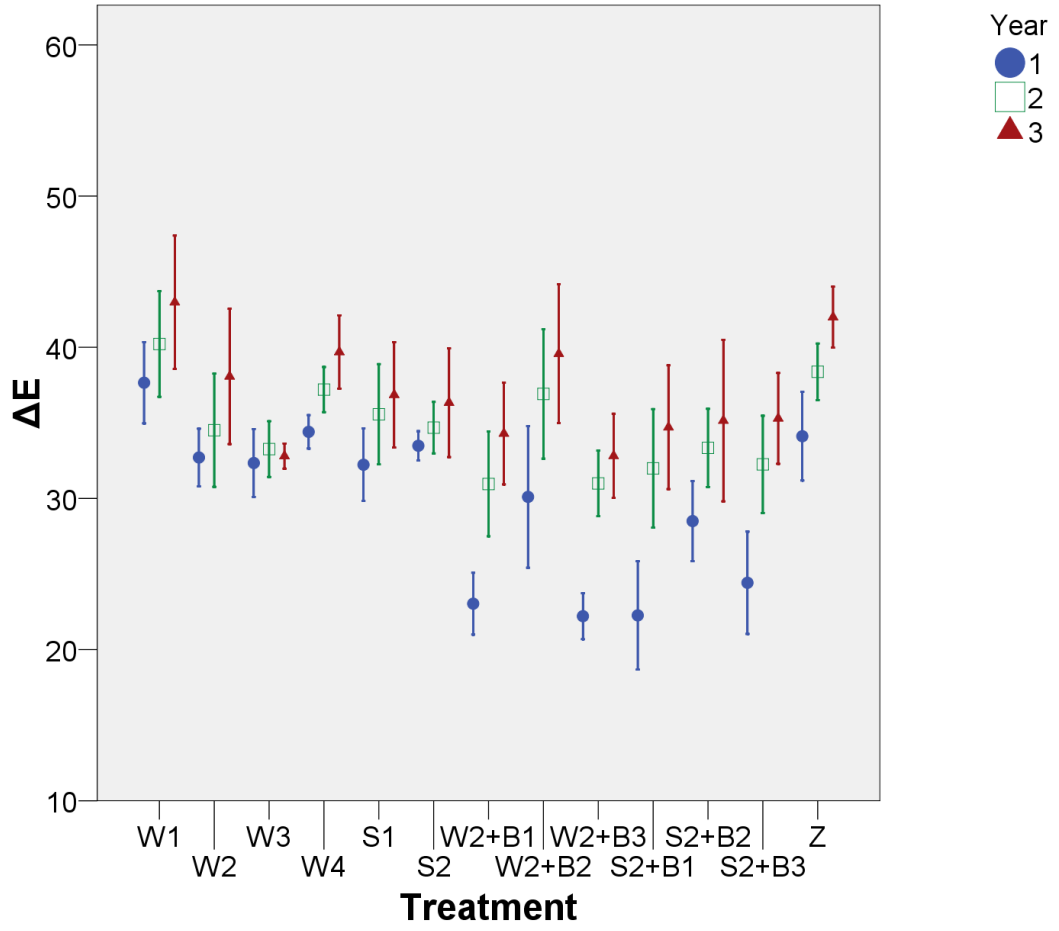

Figure 9.5: Averages and 95 % confidence intervals of the colour changer ΔE for untreated Scots pine sapwood (Z) and Scots pine sapwood dipped into an organosilicon (W1 to S2, Table 1.1) or into a combination of organosilicons W2 or S2 with biocides B1, B2 or B3 (Table 1.1) after 1, 2 and 3 years outdoor exposure at Ghent University (Belgium)

Specimens impregnated with DMS/n-OTES 1 (W1, Figure 9.6) have the largest colour difference compared to untreated and non-weathered Scots pine sapwood, while specimens impregnated with combinations of an organosilicon with B1 or B3 have the smallest colour difference. This means that the colour of these last treatments resembles the longest to untreated and non-weathered Scots pine sapwood. After two and three years the colour of these specimens approaches that of untreated and weathered Scots pine sapwood. Generally, ΔE differences become comparable for all treatments after two years

weathering and increases slightly for all specimens when weathering is continued for another year.

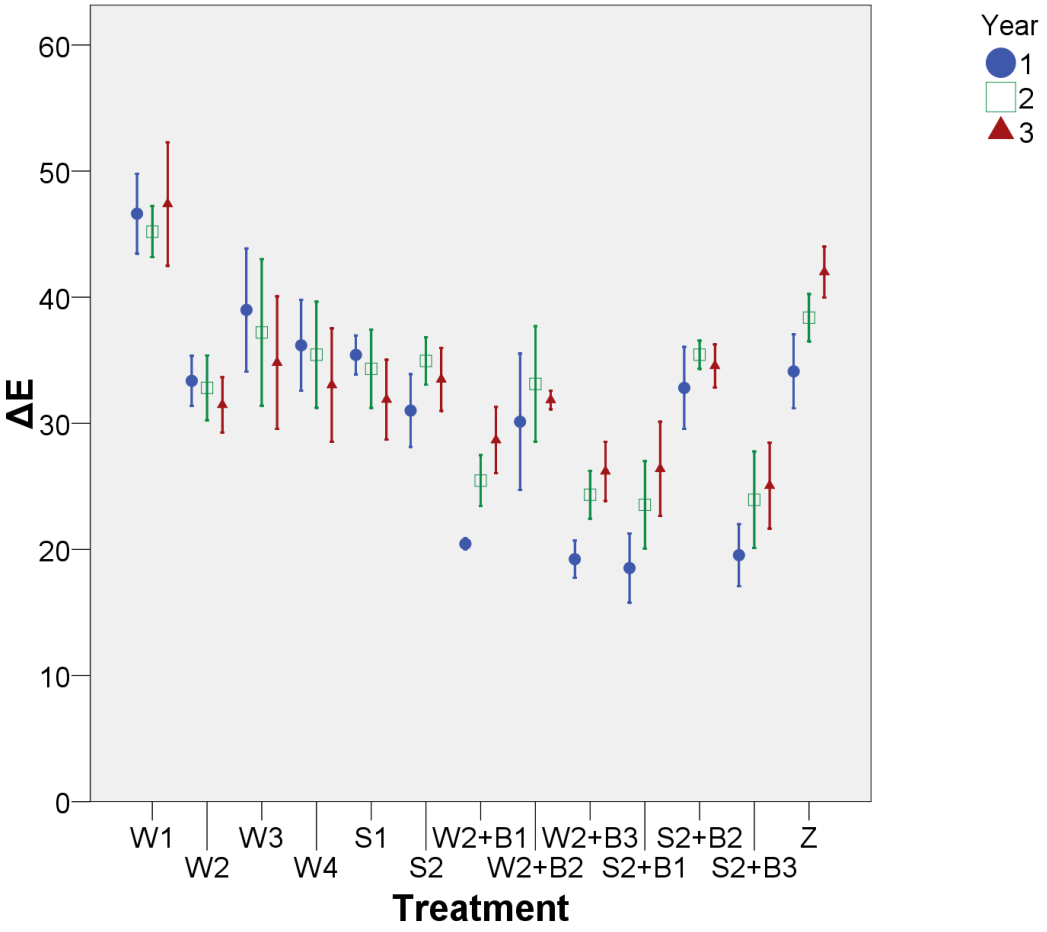

Figure 9.6: Averages and 95 % confidence intervals of the colour changer ΔE for untreated Scots pine sapwood (Z) and Scots pine sapwood impregnated with an organosilicon (W1 to S2, Table 1.1) or with a combination of organosilicons W2 or S2 with biocides B1, B2 or B3 (Table 1.1) after 1, 2 and 3 years outdoor exposure at Ghent University (Belgium)

Trying to retrieve which colour component is most influenced, L*, a* and b* values were compared with each other (data not presented). The data can be separated into a group containing untreated Scots pine sapwood and Scots pine treated with solely an organosilicon and a group containing specimens treated with a combination of an organosilicon and a biocide. While the L* value does not significantly differ within the first group, specimens belonging to the second group are much brighter, especially when treated with IPBC (B1) or

IPBC + propiconazole (B3). The trends in redness and yellowness are comparable for all specimens in that way that all values are comparable to each other regardless the exposure period, except for impregnation treatments with DMS/n-OTES 1 (W1) and impregnations involving B1 and B3, which have slightly higher a* and b* values after the first exposure year. It can therefore be concluded that mainly the L* value is responsible for the bigger variation in colour among all specimens, whereas also a* and b* contribute to the colour difference treatments with DMS/n-OTES 1 (W1) and the biocides B1 and B3 have compared to all other treatments and untreated Scots pine sapwood.

9.4 Discussion

9.4.1 Fungal evaluation

Although both laboratory and semi-industrial experiments evaluate fungal disfigurement, comparison is not straightforward. In the first experiment blue stains are the fungi leading to the disfigurement, while in the second experiment multiple factors influence the disfigurement, i.e. fungi (mainly moulds) and dirt.

Nevertheless the poor results of organosilicons as preventive agents of blue stain and mould are supported by the results found by Weigenand et al. (2006) and Ritschkoff et al. (2003). While better performance of outdoor specimens treated with a biocide containing solution is not astonishing, better performance of organosilicon impregnated specimens is remarkable. Knowing that the presence of mould fungi indicates the availability of nutrients at the wood surface (Block 1953), it can be assumed that the organosilicons, when impregnated, protect the wood surface from fast release of nutrients. This, on its turn, might be attributed to the influence organosilicons have on the moisture dynamics of the treated wood (Tshabalala et al. 2003; Donath et al. 2006a).

The diminishing effect of dipped specimens can probably be ascribed to weakening and subsequent degradation of the wood below the surface due to

weathering (Banks and Evans 1984), leading to a reduced effect of the superficially applied organosilicon. It can be stated that, except for the organosilicon plus biocide dipped specimens, the clustering of visual ratings after one year weathering already gives a good idea of the clustering after three years exposure.

9.4.2 Colour evaluation

Artificial weathering is supposed to imitate natural weathering in a fast and uniform way, trying to obtain reliable results which are easily reproducible on a standardized method. Up to now no such method uniting all these parameters has been found. Therefore care must be taken when comparing artificial and natural weathering with each other.

The initial darkening and subsequent lightening of the wood during artificial weathering can be explained by two successive processes. Because UV light (340 nm) induces the formation of free radicals and lignin is broken down while absorbing the UV light, the wood becomes darker. However, afterwards reaction products are leached out by which the wood becomes brighter again (Donath et al. 2007). Lightening of naturally exposed specimens however, seem to depend on some extra parameters, since the biocide presence influences the lightness of the treated wood considerably. Two main reasons are probably the presence of dirt and discolouring fungi at the specimens' surface. Since the specimens were washed with clear lukewarm water prior to colour measurements, it is assumed that the effect of dirt is minimised. Basically it is assumed that due to the presence of a biocide the wood surface is not so vulnerable to colonisation of discolouring fungi, leading to less darkening of the wood. The fact that also the biocide treated specimens become darker with time support this hypothesis, as it might be expected that the biocide becomes less effective due to weathering. This is further supported because darkening after one year exposure is far more distinct for dipped specimens than for impregnated specimens

The redness and yellowness values are much lower for the naturally weathered specimens after one year exposure than for the artificially weathered specimens after six weeks. Moreover they reach for nearly all treatments a constant value, supporting that most discolouration happens shortly after exposure. Certain impregnated specimens have slightly higher a* and b* values after one year exposure, indicating they are somehow protected from fast degradation, leaching or evaporation of wood components (Sjöström 1992; Grekin 2007; Salča and Fotin 2007), or from other processes induced by UV radiation (Hon 1979) which usually lead to colour change. This effect is however only temporarily and minor compared to the impact of the L* value on the total colour difference.

9.4.3 General appearance

The general appearance of weathered specimens is greatly influenced by fungal disfigurement and colour variations. Because in the laboratory experiment both parameters were investigated separately from each other, it is not straightforward to give an impression of the general appearance of the specimens. Nevertheless both the fungal and colour evaluation suggest that only when a biocide is involved in the treatment process, significant different appearance of the specimens can be expected. The natural weathering test is far more interesting, since disfigurement of both kinds was happening simultaneously on the same specimens. The test showed that the general appearance depended on several factors. The presence of a biocide influenced both parameters positively, leading to a brighter and more uniformly discoloured specimen compared to untreated Scots pine sapwood. Slight differences in colour and fungal disfigurement were present between specimens treated with different organosilicons. Regardless the composition of the treatment solution, both discolouration and fungal disfigurement were less pronounced for impregnated specimens compared to their dipped counterparts.

9.5 Conclusion

Treatment of wood with an organosilicon cannot be regarded as a form of wood modification in a strict sense, wood preservation or the application of a coating. Therefore it is not self-evident to find a method for evaluating the performance against blue staining of organosilicon treated wood whether or not in combination with a biocide. This study showed that the coating approach is more suited than the wood preservatives approach, since it is more discriminating. Secondly this research proved that under laboratory conditions an organosilicon as such is not able to protect the wood sufficiently, but combinations with biocides have good perspectives. However, outdoors the organosilicons show better resistance against fungal disfigurement than untreated wood. Obviously, the addition of a biocide enhances this effect. The discrepancy between laboratory testing and outdoor performance testing is stressed. While the former was not able to distinguish products with good perspectives from those with fewer perspectives, real outdoor performance proved significant differences are present between specimens depending on the treatment product and application technique and was more hopeful for the potential of organosilicons as part of formulations designed to protect wood surfaces under use class 3 conditions.

Acknowledgements

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10 ACCELERATED L-JOINT PERFORMANCE OF WOOD TREATED WITH ORGANOSILICON-BASED FORMULATIONS[1]

Abstract

In this research Scots pine sapwood L-joints were treated with organosilicons and organosilicons in combination with biocides. These L-joints were prepared and exposed according to the accelerated L-joint method. They were inspected each season for fungal discolouration and removed from the rack after three years outdoor exposure. Subsequently the moisture content, mass loss and decaline uptake was determined. The results show that all organosilicons are able to reduce all three parameters measured. In one case a moisture content of less than 20 % was reached, leading to no significant mass loss of the specimens. Addition of a biocide further reduced mass loss, but did not lead to such low moisture contents as when the organosilicons were applied without biocides. The outcome of the visual evaluations leads to exactly the same conclusions as the destructive testing and can therefore be regarded as a good parameter for determining the performance of the L-joints, although it is relevant to indicate that only three years field testing was covered.

[1] Submitted as:
De Vetter, L., Stevens, M., Van Acker, J. Accelerated L-joint performance of wood treated with organosilicon-based formulations. Holz als Roh- und Werkstoff

10.1 Introduction

In former days wood was the only material available to produce window joinery. Unfortunately, wood is vulnerable to weathering, leading to a changing appearance and degradation of the wood. Although these processes can be significantly slowed down by proper protection, the maintenance frequency and cost of wooden windows is nowadays for many customers a reason to choose for windows in alternative materials like aluminium or polyvinylchloride (PVC). This shift from wood to alternative materials strengthens the need for further research in the wood protection area.

Organosilicons, whether or not part of more complex preservative formulations, are tipped as products being able to prolong the service life of wood exposed under use class 3 conditions, being outdoor usage out of ground contact, such as window joinery (Mai et al. 2005; Donath et al. 2006a; De Vetter et al. 2009a, 2009b). Although several authors suggest the above-mentioned, no studies were found to support this specifically for joinery purposes. That is why in this research L-joints were produced, simulating worst case window joinery exposure. They were treated with organosilicons and combinations of organosilicons and biocides and evaluated for their performance. The basic method for evaluating the performance of L-joints is the European Standard EN 330 (1993), which was developed to determine the protective effectiveness of a wood preservative used under a coating. This method was further adapted for natural durability purposes by Van Acker and Stevens (1997) and applied in several studies (Van Acker and Stevens 2003; Timar and Beldean 2006). Since it has been shown before that the wood durability approach is better in evaluating the wood degradation of wood treated with organosilicons than the wood preservatives approach (De Vetter et al. 2009a), preference was given to the accelerated L-joint method over the standard EN 330 method.

10.2 Materials and methods

10.2.1 Preparation of test material

For above ground outdoor exposure, field testing according to the accelerated L-joint test as described by Van Acker and Stevens (1997) was chosen. Therefore Scots pine sapwood was sawn according to the dimensions given in Figure 10.1. The cross-cut end of each tenon was sealed with a two-component polyurethane system prior to impregnation. Per treatment four replicates were provided, as well as four replicates of the reference wood species Scots pine (sapwood (Z) and heartwood (Gk)), Douglas fir heartwood (*Pseudotsuga* spp., Do) and larch heartwood (*Larix deciduas*, La). The tenon members were, after being conditioned at 20 °C and 65 % relative humidity (RH), impregnated with the treating solutions using a semi-industrial scale method. Subsequent weighing of the specimens after impregnation allowed determining the product retention (Eq. 1.2). All specimens were firstly dried under ambient conditions and then further dried until constant weight at 60 °C.

A broad range of organosilicon products and combinations of organosilicons and biocides was involved in the test set-up. Three water-based macro-emulsions W1, W2 and W3 and one micro-emulsion W4 were selected, as well as two solvent-based organosilicons S1 and S2. W1 and W2 contain both dimethylsiloxane and octyltriethoxysilane (DMS/n-OTES), the first at 50 % and the second at 40 % active ingredient concentration. While W3 is a 60 % active polydimethylsiloxane (PDMS), W4 is a 100 % active mixture of PDMS and triethoxysilane (TES). Although both solvent-based organosilicons are 100 % active, S1 contains only n-OTES whereas S2 is a combination of n-OTES and methyltrimethoxysilane (MTM).

The organosilicons were diluted to an active ingredient concentration of 5 % with demineralised water or isopropylalcohol, as appropriate. Products W2 and S2 were also combined with the biocides (B1) 3-iodo-2-propynyl-butyl carbamate (IPBC), (B2) 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium

chloride (Si-Quat) and (B3) a 1:2 combination of IPBC and (±)-(cis+trans)-1-(2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl-methyl)-1H-1,2,4-triazole (propiconazole). Therefore 5 % W2 was combined with (1) 0.3 % B1, (2) 2 % B2 and (3) 0.3 % of the 1:2 concentration of B3. As a solvent-based counterpart 5 % S2 was combined with (1) 0.3 % B1 and with (3) 0.3 % B3, while (2) 10 % S2 was combined with 1 % B2. An elaborate explanation about the compositions of all organosilicons and biocides, the semi-industrial scale impregnation method and calculation methods of product retentions are given earlier in this work (1.3).

The treated tenon members were randomized together with the untreated reference tenon members and mounted per five on a common mortise beam of Scots pine sapwood as depicted in Figure 10.1. Each beam was tilted 10° to the horizontal plane to trap run-off water in the joint both from the mortise beam and the tenon member itself. To create a worst case scenario, a rock wool sponge was fixed in the joint and a water drip irrigation system released 100 ml of rain water every 24 hours, making the joint almost permanently moist. The rack to which all beams were attached is facing south-south west and is located at the outside test site of the Ghent University (Ghent, Belgium).

Due to practical circumstances the test set-up of the L-joints was done in two parts. In the first part Scots pine sapwood was treated with the six selected organosilicons and mounted outside, together with reference specimens, in the summer of 2005. In the second part of the test, the specimens were treated with the six combinations of organosilicons and biocides and with the two organosilicons W2 and S2. These tenons were mounted outside, after being randomized with new reference specimens, in the winter of 2005-2006.

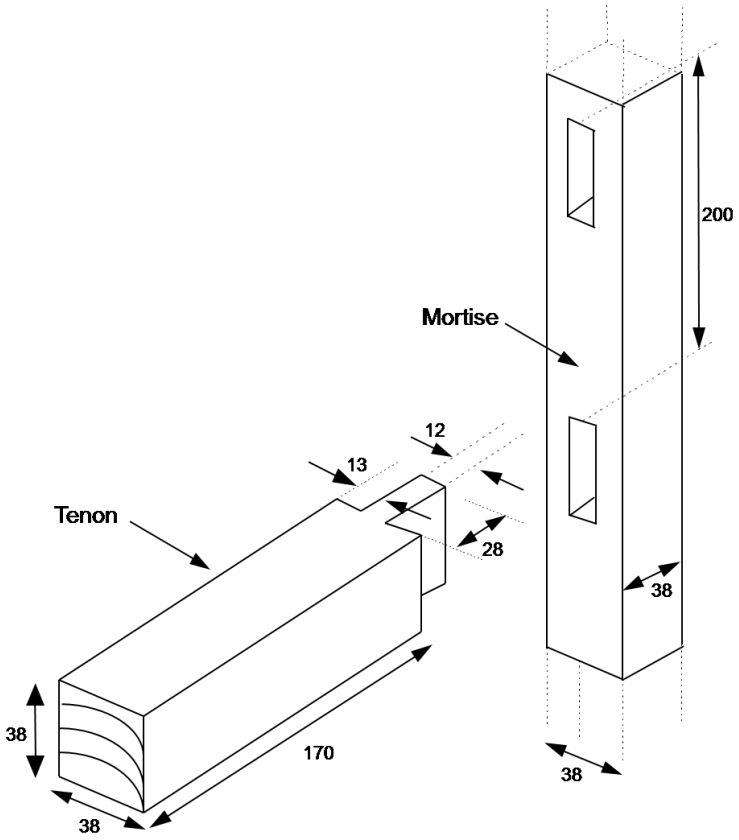

Figure 10.1: Schematic representation of the L-joint samples (mm)

10.2.2 Evaluation

The L-joint members were visited each season and inspected visually on the presence of fungal discolouration. Four ratings were given, based on the infected areas: 1: fungal discolouration of the area around the joint; 2: fungal discolouration of the area around the rock wool sponge; 3: both the areas around the joint and rock wool sponge are discoloured by fungi and 4: the entire surface area of the tenon is discoloured. A rating of 0 means no fungal discolouration was present. After three years outdoor exposure three out of four replicates of each treatment/reference wood species were removed from the mortise beams and subsequently sawn according to the scheme presented in Figure 10.2. Two main locations were analysed: position 1 is close to the sealed cross cut whereas position 2 is close to the joint.

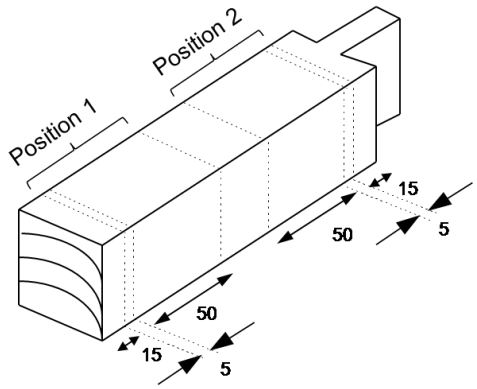

Figure 10.2: Sawing scheme of an L-joint tenon (mm)

The bigger blocks measuring 50 × 38 × 38 mm were used to determine the moisture content (MC, Eq. 10.1) and mass loss (ML, Eq. 10.2) at both positions 1 and 2. Therefore the blocks were weighed immediately after sawing (M_{wet}) and subsequently slowly dried to 103 °C and weighed again ($M_{103°C}$).

$$MC\ (\%) = \frac{M_{wet}\ (g) - M_{103°C}(g)}{M_{103°C}\ (g)} \times 100 \tag{10.1}$$

$$ML\ (\%) = \frac{\frac{M_{prior\ to\ exposure}\ (g)}{Volume_{tenon}(cm^3)} - \frac{M_{103°C}\ (g)}{Volume_{block}\ (cm^3)}}{\frac{M_{prior\ to\ exposure}\ (g)}{Volume_{tenon}\ (cm^3)}} \tag{10.2}$$

Since Carey et al. (1981) stated that permeability increase can be regarded as being the first detectable indication of attack of the wood, it was found valuable to determine this parameter. Therefore the small blocks (5 × 38 × 38 mm) were first dried and cooled down to 50 °C, after which they were dipped for ten seconds in decaline (decahydronaphtalene). Weighing the samples prior to and after dipping allows to calculate the permeability as proposed by Van Acker and Stevens (2003) (Eq. 10.3).

$$decaline\ uptake(kg/m^3) = \frac{M_{after\ dipping}(g) - M_{before\ dipping}\ (g)}{Volume_{section}\ (cm^3)} \times 1.000 \tag{10.3}$$

10.3 Results and discussion

10.3.1 Loadings

Table 10.1 gives an overview of the product retentions obtained by semi-industrial impregnation of Scots pine sapwood L-joint specimens with the organosilicon (and biocide) treating solutions.

Table 10.1: Product retention of organosilicon (W and S) and biocide (B) due to impregnation of Scots pine sapwood L-joints (average ± standard deviation, kg/m³)

Product	Product retention
W1	55.1 ± 18.4
W2	93.8 ± 5.0
W3	59.3 ± 5.7
W4	32.1 ± 1.5
S1	26.6 ± 2.4
S2	28.9 ± 3.4
W2 + B1	(33.4 ± 27.1) + (4.7 ± 3.8)
W2 + B2	(54.0 ± 2.8)+ (12.0 ± 0.6)
W2 + B3	(60.0 ± 2.9) + (28.8 ± 1.4)
S2 + B1	(15.3 ± 0.6) + (5.4 ± 0.2)
S2 + B2	(30.4 ± 0.9) + (4.2 ± 0.1)
S2 + B3	(15.4 ± 0.6) + (18.5 ± 0.7)
W2	58.7 ± 5.0
S2	18.8 ± 0.5

10.3.2 Visual assessment

Tables 10.2 and 10.3 give an overview of the visual ratings of all exposed tenons per season. The ratings start at the first season after the specimens have been put outside, since at the start of the test all specimens were rated 0, meaning no fungal discolouration was present. For the specimens of the first part of the test this was autumn 2005 (Table 10.2), while for the second part this was spring 2006 (Table 10.3).

As is clearly shown in both tables certain wood species/treatments perform far better than others. The best results are obtained for the reference wood species

larch (La), Douglas fir (Do) and Scots pine heartwood (Gk). The sometimes lower rating of one or more replicates is because the tenons were not always made of 100 % heartwood. Instead, approximately one third sapwood was included, as commonly used in practice. As could be expected do tenons treated with biocides perform better than untreated Scots pine sapwood. Table 10.3 shows that they behave equal as the reference wood species, although treatment with W2 + B1 shows somewhat lower ratings. In any case, both tables indicate that treatments with solely an organosilicon improve the performance of the tenon already significantly. Treatment with W3 even makes the tenons behave as well as the reference wood species. Treatments with S1 and W1 principally only seem to delay fungal discolouration with 3 and 1.5 year, respectively. These results are a confirmation of what was found for fungal disfigurement of wood exposed outdoors under EN 927-3 (1996) conditions (Chapter 9). It can thus be concluded that (1) organosilicons, when impregnated, can reduce fungal disfigurement of Scots pine sapwood significantly and that (2) addition of biocides further improves the performance.

Although it has been reported that visible decay is not affected significantly by the month in which the trials were first exposed (Carey 2002), it is striking that the untreated Scots pine sapwood specimens exposed in the summer of 2005 were completely discoloured already after one season (autumn 2005), while only three out of four untreated Scots pine sapwood tenons exposed from the winter of 2005-2006 on were completely discoloured by fungi after approximately 9 months (autumn 2006).

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Table 10.2: Number of specimens attributed to visual rating classes 0 (no fungal discolouration present) to 4 (L-joint is completely discoloured) of outdoor accelerated L-joints treated with organosilicons (W and S) and reference L-joints (Z, Gk, Do and La) (10.2.1, autumn 2005 = 3 months exposure)

	2005					2006																					2007																	2008									
	autumn					winter					spring					summer					autumn					winter					spring					summer					autumn					spring					summer				
	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4
W1		3		1		1	2			1	3				1	2	1	1			1				3					4					4					4					4					4		1	1	2					4
W2		4				2	2				4					3				1	2			1	1	2		2			2		2			2	1	1			3		1			3		1			4				
W3	3	1				4					4					4					4					4					4					4					3		1			4					4				
W4	2	2				4					3	1				2			1	1	2				2	2		1		1	1	1	1		1	2		2			2	1	1			2		2			3		1		
S1		2		2		2	1	1			4							2	1	1	1				3			1		3	1		1		2			1		3				2	2			1	2	1				1	3
S2	2	2				4					2	2				4					4					3				1	3				1	3		1			4					3			1		3		1		
Z					4					4	1				3			1		3					4					4				1	3					4					4					4					4
Gk	4					4					4					4					4					4					4					4					4					4					4		2		2		
Do	3			1		4					4					4					4					4					4					4					4					4					4		3		1		
La	3		1			4					4					4					4					4					3		1			4					4					4					4					4	

Table 10.3: Number of specimens attributed to visual rating classes 0 to 4 of outdoor accelerated L-joints treated with organosilicons (W and S) and biocides (B) and reference L-joints (Z, Gk, Do and La) (10.2.1, spring 2006 = 3 months exposure)

	2006															2007																						2008														2009				
	spring					summer					autumn					winter					spring					summer					autumn					spring					summer					autumn					winter				
	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4
W2 +B1	4					4					4					4					4					4					3		1			3			1		2		1	1						3				1
W2+B2	4					4					4					4					3		1			4					4					4					3		1								4				
W2+B3	4					4					4					4					4					4					4					2	2				4										4				
S2+B1	4					4					4					4					4					4					4					3	1				4										3			1	
S2+B2	4					4					4					4					4					4					2	1			1	3		1			4										3	1			
S2+B3	4					4					4					4					4					3	1				4					4					4										3	1			
W2	4					4					4					4					3	1				2	1		1		3		1			1	1		2		1		2	1								1		1	2
S2	4					4					4					3		1			4					4					3		1			3			1		3		1								3	1			
Z	4					1		1	1	1			1		3	2		1		1			2	1	1			1	1	2			1		3				1	3				1	3							1				3
Gk	4					4					4					4					4					4					4					3	1				4										3		1		
Do	4					4					4					4					4					4					4					4					4										4				
La	4					4					4					3		1			4					4					4					4					4										3	1			

The differences in visible fungal discolouration as mentioned above, caused by moulds, blue stains, soft rot fungi and basidiomycetes together, being clear for the different tenons, do not allow predicting the long-term performance. In the succession of degradation of outside exposed wood, fungal discolouration is a precursor of wood decay. Although it is shown before that there is no clear correlation between the early stages of decay and the long-term performance (Carey 2002) it is evident that the treatments without fungal discolouration after three years exposure will have a longer period without failure through decay

10.3.3 Permeability

The first signs of fungal degradation of wood can be seen by increased porosity based on altered decaline uptake. Lower decaline uptake indicates limited fungal attack. Table 10.4 shows the decaline uptake for the tenons of the two test set-ups after three years outdoor exposure and for Scots pine sapwood which has not been exposed outside, but stayed in the conditioning room during that time.

Comparing the exposed to non-exposed Scots pine sapwood specimens shows a major increase in decaline uptake, denoting fungal decay. This is also the case for all treated specimens, although to a lesser extent, indicating some protective effectiveness of the organosilicons (and biocides). Moreover specimens treated with 5 % active PDMS (W3) and with 5 % DMS/n-OTES plus 2 % Si-Quat (W2 + B2) have a comparable decaline uptake after three years exposure as non-exposed Scots pine sapwood. This suggests only minor fungal attack and subsequently mass loss. As could be expected the highest uptake is noted at position 2, being closest to the joint and this for all exposed specimens. The reported values are similar to those reported by Van Acker and Stevens (2003) and Van Acker (2001), although their reported values are after only 18 months exposure.

Table 10.4: Decaline uptake (kg/m³) of cross sections far from (position 1) and close to (position 2) the joint of L-joints after three years accelerated exposure compared with control specimens

Material	Part	Position 1	Position 2
Treatment			
W1	1	326	328
W2	1	235	324
W3	1	93	121
W4	1	240	315
S1	1	239	336
S2	1	162	278
W2 + B1	2	255	372
W2 + B2	2	123	138
W2 + B3	2	159	237
S2 + B1	2	295	375
S2 + B2	2	361	370
S2 + B3	2	258	331
W2	2	241	341
S2	2	252	334
Untreated controls			
SP sapwood	1 / 2	379 / 437	419 / 459
SP heartwood	1 / 2	57 / 73	80 / 78
Larch heartwood	1 / 2	75 / 140	92 / 125
Douglas fir heartwood	1 / 2	124 /140	138 / 155
SP sapwood	Not exposed	145	133

10.3.4 Moisture content and mass loss

Moisture contents and mass losses are presented in Figures 10.3 and 10.4 for the tenons of the first and second part of the test, respectively. Both figures show that the moisture content is always higher at position 2 than at position 1. This seems logic, since position 1 is furthest from the joint and position 2 is closest to the joint and partly under the rock wool sponge. Knowing that moisture content provides an indication of development of hazard and its spread in the tenon, higher mass losses are to be expected at position 2 compared to position 1 (Carey et al. 1981). Furthermore the figures indicate that untreated Scots pine sapwood always has the highest moisture content, and this on both positions. This means that the organosilicons are able to reduce the moisture content of the exposed tenons. Most organosilicons succeed in reducing the moisture content with one third to even more than half. The reduction is most significant at position 1. Remarkable is the observation that

addition of a biocide to the treating solution leads to a lower reduction in moisture content of the tenons compared to the corresponding treatment without biocide (Figure 10.4). An exception is the combination W2 + B2.

Treatment of Scots pine sapwood with W3 (PDMS) is the only treatment which is able to reduce the moisture content at both positions below 20 %, being the minimum moisture content needed for fungal decay by basidiomycetes (Figure 10.3). It is therefore not surprising that these tenons hardly show any mass loss, as was expected based on decaline uptake. Five per cent mass loss was considered as the limit for reliability of the calculation of the estimated mass loss (Van Acker and Stevens 2003). Also the treatment of Scots pine sapwood with W2 (DMS/n-OTES) reduces the mass loss below (position 1) or just above 5 % (position 2). Although based on laboratory experiments, it was suggested that organosilicons could be able to protect Scots pine sapwood from fungal attack when impregnated at low concentrations and exposed under use class 3 conditions (De Vetter et al. 2009a). The results as presented here for outdoor field testing support that finding.

A slight reduction in mass loss is found for tenons treated with W1 or S2, while W4 and S1 do not seem to influence the mass loss, although the moisture content is reduced. However, when a biocide is added to the treating solution, even lower mass losses are recorded (Figure 10.4). These outside performance tests are therefore in agreement with laboratory basidiomycetes tests showing higher reduction in mass loss due to the addition of a biocide to an organosilicon treatment solution. Furthermore it confirms the effectiveness after leaching, in this case natural leaching contrary to EN 84 leaching in De Vetter et al. (2009b).

The mass losses found in this research for untreated Scots pine sapwood after three years exposure are in between values reported by Van Acker et al. (2003) for untreated Scots pine sapwood exposed under comparable exposition and at the same location, and evaluated after 18 months and 4 years exposure.

However, the mass losses of Scots pine heartwood are in underlying research higher than in the above mentioned study. This might be attributed to the Scots pine sapwood present in the tenons. Although it is reported that the use of simple water repellent treatments alone, without active ingredients, may not provide sufficient effective protection against decay in an L-joint outdoor exposure test (Derbyshire and Carey 2001), this research found two organosilicons (W3, PDMS and W2, DMS/n-OTES) who succeeded in reducing the mass loss below 5 % and can therefore be considered effective.

Moisture content of Scots pine sapwood exceeding 100 % is reported to be in line with high mass losses and attributed to either water being a degradation product from decay or by total loss of moisture control in fully decayed wood (Van Acker and Stevens 2003). This could also be the case for the untreated or with W1 treated Scots pine sapwood in this research.

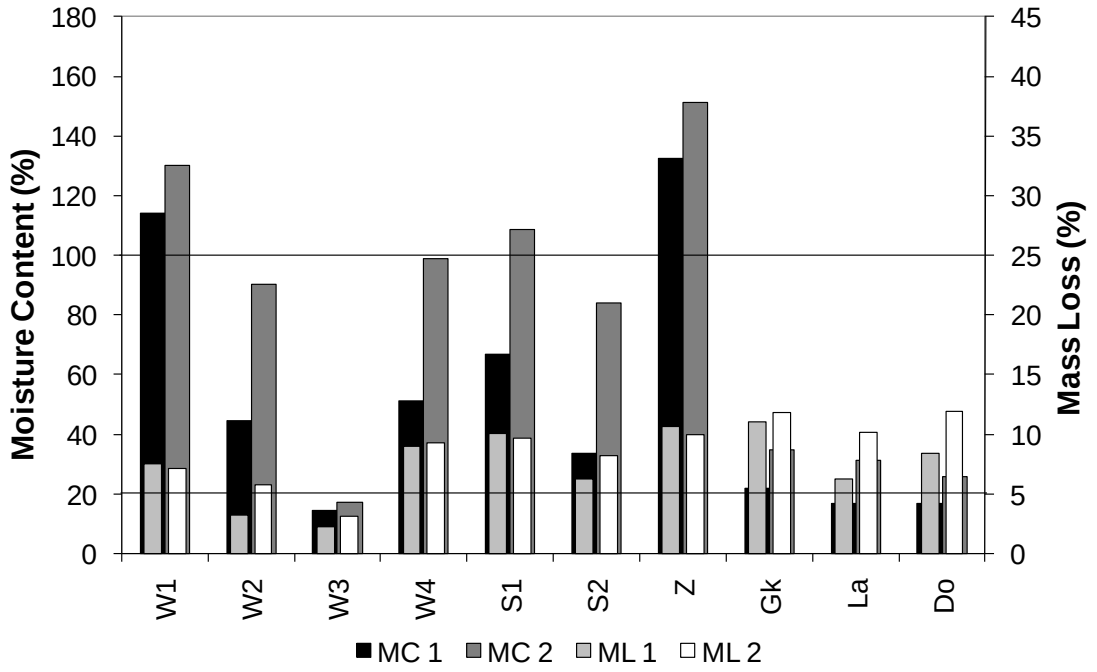

Figure 10.3: Moisture content (MC) and mass loss (ML) of accelerated L-joints exposed for three years at the outside field test site of Ghent University (Belgium) and evaluated at positions far from (1) and close to (2) the joint. The Scots pine sapwood specimens were impregnated with organosilicons W1 to S2 or left untreated (Z). Reference heartwood specimens of Scots pine (Gk), Douglas fir (Do) and larch (La) were added

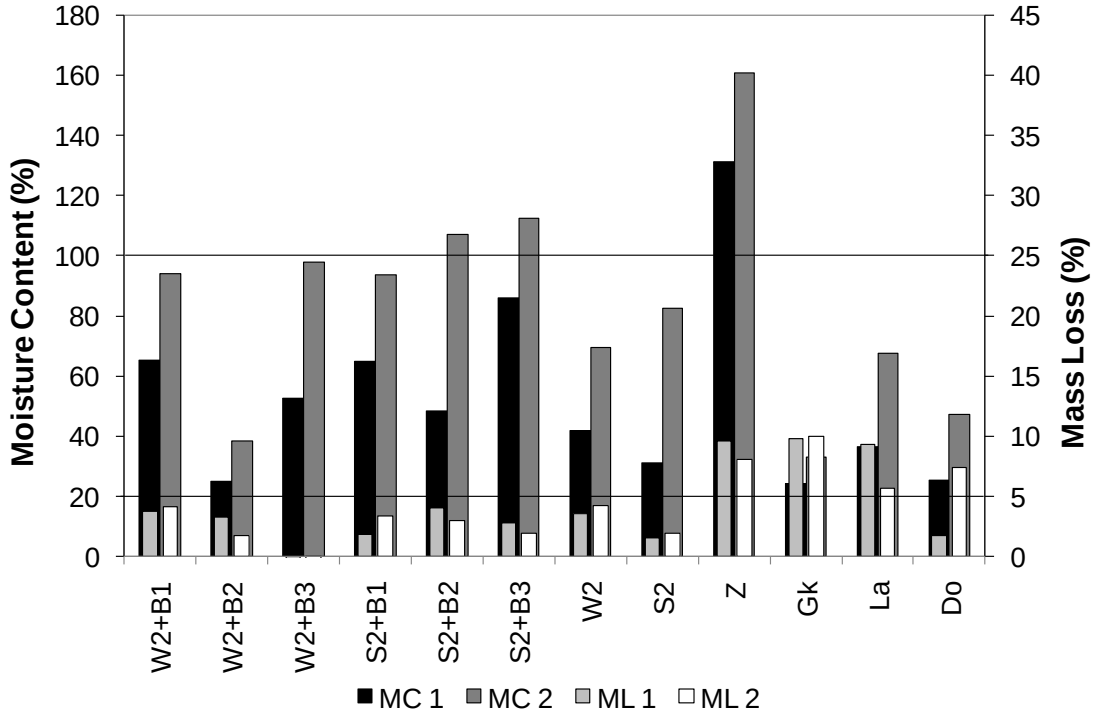

Figure 10.4: Moisture content (MC) and mass loss (ML) of accelerated L-joints exposed for three years at the Laboratory of Wood Technology (Belgium) and evaluated at positions far from (1) and close to (2) the joint. The Scots pine sapwood specimens were impregnated with organosilicons W2 or S2, with combinations of organosilicons W2 and S2 with biocides B1, B2 or B3 or left untreated (Z). Reference heartwood specimens of Scots pine (Gk), Douglas fir (Do) and larch (La) were added

10.3.5 Confronting visual assessment and destructive analyses

Ranking the treatments from best performing to worst performing, including untreated Scots pine sapwood, leads to exactly the same ranking when based on the visual assessment or when based on destructive analyses leading to decaline uptakes, moisture contents and mass losses and can be represented as follows:

Biocide containing treatments ≈ W3 > W2+B1 > S2 > W2 > W4 >> S1 > W1 > untreated Scots pine sapwood (Z)

However when also the heartwood reference tenons of Scots pine, Douglas fir and larch are included a big discrepancy is seen between at the one hand visual assessments and decaline uptake and at the other hand moisture contents and mass losses. While visually no discolouration is seen and decaline uptake is low, the mass losses are above the 5 % level. It is assumed that part of the mass losses can be ascribed to losses of wood components due to leaching. The treated specimens were leached during impregnation, while the reference specimens were not leached prior to the first exposure.

10.4 Conclusion

This study is the first reporting performance of organosilicon (and biocide) treated Scots pine sapwood L-joints. Up to now mainly laboratory experiments were performed, in which the organosilicons, when applied at low concentrations, could not guarantee sufficient protection to the wood. Nevertheless it was stated that they could contribute to the protection of wood when used outside, out of ground contact. This is confirmed in this study, where organosilicon treatments of L-joints showed reduced fungal discolouration, decaline uptake, moisture content and mass loss after three years accelerated exposure. Addition of a biocide further lowered fungal discolouration and mass loss, although the moisture content was reduced to a lesser extent. This research therefore further stresses that organosilicons can definitely contribute to better performance of wood exposed under use class 3 conditions.

Acknowledgements

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Discussion

In the first chapter it was discovered that when wood was treated with low concentrations of organosilicons, no improvement in the examined wood-water related properties could be detected with the laboratory experiments. Therefore, by analogy with fungal efficacy, application of highly concentrated organosilicons was found necessary. However, since Part II already stated that full cell impregnation with organosilicons is economically not feasible; preference was given to treat only the surface with high concentrations of organosilicons. This approach was worthwhile, since lower uptake of water could be demonstrated for organosilicon treated solid Scots pine.

Not only solid wood is being used in use class 3 applications, but also wood-based materials like plywood. Therefore the same approach was used to verify whether they could benefit from envelope treatment with organosilicons. Although the study learned that reduced water uptake was achieved, the organosilicons lost functionality after weathering, as was the case for solid wood. Besides the entire envelope of the material also the cross cuts could be protected from water ingress. This was investigated also for MDF and OSB. In contrast however these re-engineered materials behaved opposite: more water uptake was seen on treated material compared to untreated material. Both the macro- and microscopic structure of the materials differ greatly from solid wood and this is expressed in its water behaviour. To gain more insight further research is needed, but this is out of the scope of this work.

All laboratory tests performed up to now revealed only poor performance of organosilicon treated wood. Since laboratory conditions are harsh it was found necessary to verify the results by real outdoor exposure of wooden elements. In a first attempt cladding was simulated and this both in the laboratory and outside. Again it was found that the wood preservatives approach was not the best suited to evaluate the performance, leading to the conclusion that new methodologies are necessary to evaluate new wood treatment products. Under outdoor exposure conditions however, organosilicon impregnated wood showed

much less fungal discolouration compared to untreated wood. Addition of biocides enhanced this, and lead to less discolouration, although also this effect lowered with continued weathering.

Finally organosilicon impregnated L-joints were mounted and evaluated after three years outdoor exposure. They behaved better in all examined parameters compared to untreated L-joints. The addition of biocides further reduced fungal discolouration, although the moisture content was not lowered to the same extent as when organosilicons were applied alone. Both outdoor exposure tests confirmed that organosilicons can contribute to better performance under use class 3 conditions. However reduced effectiveness was noted after weathering.

GENERAL CONCLUSIONS

11 General conclusions

Wood is a natural material susceptible to weathering and degradation. Therefore efforts are undertaken to avoid or at least postpone these phenomena. Since the public awareness of the use of biocides and other potentially harmful components to the environment is increased, environmental friendly treatments of wood are considered as alternatives. Water repellents are suitable options and since organosilicons proved effectiveness on mineral substrates and are considered safe, they are put forward as a group of chemicals potentially suited for the job.

The rationale of this dissertation was to find out whether organosilicons can prolong the service life of wood used outdoors, out of ground contact. Therefore a large range of organosilicons with changing properties was chosen. Several methods were applied to obtain information on the position and amount of organosilicons present in treated wood, the durability and ecotoxicity of the obtained product and the appearance and outdoor performance of small-scaled samples. Therefore this dissertation was split into three parts.

In the first part focus is on methods tracing organosilicons in treated wood. SEM-EDX analysis was used and this was combined with a non-destructive 3D visualization technique based on micro-CT scanning. The combination of these techniques was considered very valuable and with the prospect of the even more precise nano-CT the possible applications in wood research can only increase. This is however not equally evident for the quantitative determination technique based on the molybdenum blue method. The technique was developed for detecting inorganic silicon and its adaptation for organic silicon does not seem straightforward. The destruction phase transforming organic silicon into inorganic silicon seems to be tricky and will most likely need to be done in several steps, including pre-treatment with alcoholic substances.

The first parameters of the treated wood to be characterised in the second part of this work were durability and ecotoxicity. A dose-response curve was determined between concentration of organosilicon applied and efficacy against wood rotting fungi. Interpreting the results using the wood preservatives approach only leads to extremely high concentrations being adequate. The natural durability approach however seems more suited and leaves better options for organosilicons as agents in protecting wood against fungal degradation. Nevertheless a better option seems to be combining the organosilicons in experiments with biocides. It was found valuable to elaborate on methodology combining sufficient protection against wood destroying organisms while safeguarding the environment from toxic substances. Afterwards the ecotoxicity of wood leachates was determined in order to see whether organosilicons could contribute to reduce leaching of biocides. While the efficacy of the biocides was not altered, the ecotoxicity of their leachates against *Daphnia magna* didn't change either. Resuming organosilicons do not protect biocides significantly from leaching out of wood.

Although the use of organosilicons as protecting agents for wood should take into account some constraints as concluded from research performed in the second part of this dissertation, the conditions set were used in field tests in the third and final part of this work. First the interaction between treated wood and water was thoroughly investigated following several methodologies. Anti swelling and anti shrinkage efficiency, water repellent effectiveness and moisture content were determined on impregnated solid wood specimens using both static as well as dynamic methods. None of these studies gave satisfactory results showing that organosilicons at the concentrations applied could positively influence the wood-water balance. The same conclusion was drawn when re-engineered materials like MDF or OSB were treated with organosilicons and subjected to a floating test. Nevertheless some positive results were seen when solid wood and plywood were considered. Recalling that biocide addition might be necessary to grant sufficient biological effectiveness, test specimens simulating cladding and window corners were

prepared and treated with organosilicons, both as such and in combination with biocides. Results of these field tests were compared with laboratory scaled analyses and led to some interesting conclusions. Firstly, organosilicon treated material behaves far better when exposed outdoors than might be expected from laboratory experiments. This underpins the necessity of field-testing since laboratory experiments as performed nowadays cannot, and will probably never, be able to replace field testing. Secondly, certain organosilicon treatments induce wood to perform similar as reference materials which are traditionally considered having a fit for purpose service life. And thirdly the addition of a biocide improves the biological performance substantially.

11.1 Determining Si in wood

Organosilicon compounds penetrate the wood matrix and bring new substances inside wood. To have better insight on the exact location where these products polymerize, analyses are detailed in **chapter 2** using an energy dispersive X-ray spectrometer (SEM-EDX) combined with non-destructive 3D X-ray micro-computed tomography (micro-CT). Both softwood and hardwood were dipped and impregnated with an organosilicon. The SEM-EDX images revealed that when wood was dipped in the organosilicon, the product was mainly found in the lumen or as a thin layer on the wood cell walls. Most signals were found in the tracheids of the earlywood and the wood rays. These props or this layer was not inextricably connected to the wood. The micro-CT was able to clearly identify the penetration front of the organosilicon and confirmed the location inside tracheids and lumens. Concerning impregnated wood, SEM-EDX showed that the organosilicon penetrated the cell walls. Combination of these images with micro-CT information learned that the organosilicon was found over the entire wood block and had the highest concentrations at the borders of the block and in the wood rays. Combining both scanning techniques therefore seems very promising for detecting Si, originating from organosilicon treatment, inside wood.

In **chapter 3** a quantitative analysis method based on the molybdenum blue method was validated as a method to determine the amount of silicon present in (un)treated wood. This revealed that the most crucial and difficult part of such analysis is the first part, transforming organic silicon into inorganic silicic acids. Although literature claims the method to be suited for analyses of Si and SiO_2 in woody material like bamboo, the method did not give satisfactory results on wood treated with organosilicon compounds. It was therefore concluded further research is needed to adopt the method to be reliable in determining the silicon content of organosilicon treated wood.

11.2 Laboratory assessment of the efficacy and impact of organosilicon treatments

At first was examined whether organosilicon treatments of wood had a significant influence on the decay rate and durability of wood. Therefore wood was treated with concentration ranges of different organosilicons and exposed to common wood destroying test fungi. The results presented in **chapter 4** reveal increasing protective capacity with increasing weight percent gain. Even full preservative effectiveness could be reached with certain products. This was however only possible at very high weight percent gains, presently being not cost-effective. Since the focus of this work is on usage under use class 3 conditions, the results were also interpreted with the natural durability approach. This time more products showed potential to protect wood at lower concentrations of organosilicons. Further testing at such lower concentration levels however showed that only a limited number of organosilicons was able to protect wood effectively for the envisaged use class.

Subsequently it was found interesting to elaborate on methodology combining efficacy against wood rotting fungi and ecotoxicity of wood leachates. Since both parameters are important for preservative treated as well as modified

wood, wood products of each of these groups were used as test materials in the research, next to untreated reference wood species. All materials were leached according to both a harsh and a mild leaching regime and this each time at two harvesting periods. A tiered approach for evaluating the ecotoxicity of these leachates for *Daphnia magna* was set up. **Chapter 5** shows that this was successful in detecting differences in toxicity behaviour between preservative treated and modified wood. Whereas the toxicity of leachates of preservative treated wood decreases over time and from the harsh to the mild leaching procedure, the toxicity of modified wood leachates was only influenced by the leaching procedure. Comparing the results of efficacy and ecotoxicity testing shows that products performing well for one parameter score worse for the other parameter. The research however also indicated that improving one parameter by changing i.e. the concentration of the product or a process parameter is possible without compromising to the other parameter.

In **chapter 6** lower concentrations of organosilicons, which were assumed to be economically feasible, were combined with preservatives with known effectiveness and evaluated according to the method explained above. Wood treated with solely organosilicons, biocides and combinations of both were all leached to simulate ageing and subsequently exposed to wood rotting fungi. As could be expected only some organosilicons improved the durability with one or two classes, while all biocides easily reached durability class 1. This was also the case for combinations of organosilicons and biocides, indicating organosilicons do not have a negative impact on the effectiveness of the biocides. Major drawback to this was however related to the ecotoxicity of the leachates of the treated wood. Regardless the leaching method used and the time of harvesting of the leachates, no significant difference in toxicity towards the crustacean *Daphnia magna* could be found between wood treated with solely biocides or in combination with organosilicons. This stresses the poor ability of organosilicons in reducing leaching of biocides from treated wood.

11.3 Moisture dynamics as basis for performance of organosilicon wood treatments

Since organosilicons are known as water repellents on mineral substrates and since wood is a hygroscopic material, changes in the wood-water relationship were expected when wood is treated with organosilicons. **Chapters 7 and 8** disclose different aspects of the wood-water relationship on laboratory scale. In Chapter 7 focus was on the behaviour of vacuum impregnated solid wood while Chapter 8 deals with envelope treated solid wood, wood-based panels and re-engineered wood products. Although several aspects of the wood-water relationship were investigated, none of them was significantly better for organosilicon impregnated solid wood compared to untreated wood. For envelope treated OSB and MDF even worse performance had to be noticed compared to untreated material. However, improvements were present for solid wood and plywood when organosilicons were applied highly concentrated onto the envelope of the material. Unfortunately the effectiveness of the treatment diminished considerably after weathering.

Since outdoor performance tests are considered indispensable as a supplement to laboratory experiments, in **chapter 9** the general appearance and weathering performance of organosilicon treated cladding was examined. Both laboratory tests using artificial weathering as well as outdoor experiments using natural weathering were performed. Fungal discolouration and colour change were evaluated in both cases. Several methods estimating blue staining of laboratory specimens were compared, leading to the conclusion that a coating approach is more suited than a wood preservatives approach. However, sufficient protection could only be guaranteed when a biocide was included in the treatment. This is in contrast with outdoor performance evaluation, where both organosilicon and biocide treated wood had better appearance than untreated wood. While artificial weathering led to uniformly discoloured specimens, more diversity was seen among the naturally weathered specimens.

Elaborating on outdoor testing under use class 3 conditions, L-joints (simulated window corners) were prepared, treated and exposed outside using accelerated test conditions. The fungal discolouration was rated every season and the specimens were removed from the rack after three years exposure. Subsequently the permeability, moisture content and mass loss were determined. All examination methods showed the same order of best to worst performing treatments and confirm the results obtained in chapter 9. It can be concluded that organosilicons can significantly improve the performance of the L-joints and this by reducing the moisture content, fungal discolouration and mass loss. Addition of a biocide to the treating solution further enhances these effects, except for the moisture content, which is reduced to a lesser extent than when organosilicons were applied alone. In **chapter 10** it is therefore concluded that organosilicons can play a role in formulations aiming to protect wood under use class 3 conditions.

11.4 General remarks and future research

Resuming, when seeking for an environmental friendly product which can protect wood exposed outside out of ground contact, organosilicons may not be disregarded. Table 11.1 gives an overview of the performance of organosilicon treated Scots pine sapwood compared to untreated wood. To be able to compare the results as much as possible preference was given to report on those tests where the organosilicons were applied at 5 % active ingredient concentration. The table shows that despite equal performance of treated and untreated wood in laboratory methods, field tests show organosilicon treated wood generally outperforms untreated Scots pine sapwood. Secondly water-based emulsions may perform at least as good as solvent-based solutions. Furthermore could no better performance be observed for the micro-emulsion W4 compared to the macro-emulsions. Concerning all products the 60 % active PDMS (W3) seems to have the most potential, based on the outdoor field

Table 11.1: Overview of performance of at 5 % ai organosilicon treated Scots pine sapwood compared to untreated wood and evaluated for several parameters

Test	Laboratory testing									Field testing							
	Dura-bility	Ecotoxi-city	Water-uptake	Vapour-uptake		DVS	UV-CON	Blue stain	UV-2000	Outdoor cladding				L-joint			
Para-meter[1]	DC	TU	WRE ASE AsE	WRE	ASE AsE	Mass change	MC	Fungal discolour-ration	ΔE	Fungal discolour-ration		ΔE		Fungal discolour-ration	Deca-line uptake	MC	ML
Treat-ment[2]	I	I	I	I	I	I	D	D	D	D	I	D	I	I	I	I	I
W1	≈	≈	≈	≈	-			≈	≈	≈	≈	≈	+	≈	≈	≈	+
W2	+	≈	≈	≈	-	≈	≈	≈	≈	≈	+	≈	≈	++	+	+	++
W3		≈	≈	≈	-	≈	≈	≈	≈	+	+	≈	≈	++	++	++	++
W4	++	≈				≈	≈	≈	≈	≈	+	≈	≈	++	+	+	≈
W5	≈					≈	≈										
S1	≈	≈				≈	≈	≈	≈	≈	+	≈	≈	≈	+	+	≈
S2	+	≈				≈	≈	+	≈	+	+	≈	≈	+	+	+	+

[1]: details on parameters: DC: durability class; TU: Toxic Unit; WRE: Water repellent effectiveness; ASE / AsE: Anti swelling and shrinkage effectiveness; MC: Moisture content; ΔE: Colour change; ML: Mass loss

[2]: details on treatments: D: dipping; I: impregnation; details on products are given in Table 1.1

-: performance is worse compared to untreated Scots pine sapwood; ≈: performance is comparable to the performance of untreated Scots pine sapwood; +: performance is better compared to untreated Scots pine sapwood; ++: performance is much better compared to untreated Scots pine sapwood and/or meets the criterion for usage in use class 3 applications

testing results. When pursuing use of organosilicons as such, and their use in combination with biocides as more complex formulations.

This dissertation points at some difficulties in evaluating organosilicon treated wood, and leaves options for future research. It was shown that organosilicons cannot be regarded as wood preservatives or as coatings and that treatment of wood with those products is no wood modification in the strict sense. However the methods most often used to validate a product are based on European Standards, which did not prove to be efficient in evaluating organosilicon treated wood. This was especially the case for methods designed for evaluating wood preservatives, while methods created to determine natural durability were better suited. When continuing on the route of wood protection with organosilicons, methods should be developed to properly measure their potential. These methods could be based on existing standards, but need adaptation.

This necessity is further stressed when laboratory results are compared to outdoor field testing. A discrepancy between the results was noted, leading to the need of adopted laboratory tests, or the inevitable field tests, which are a lot more time consuming and consequently more expensive. This need for further development of methods is not restricted to durability testing, but is also valid for simulating fungal disfigurement and gaining information on wood-water relationships.

As a basis for developing new methods, more fundamental knowledge should be gathered on the interaction between organosilicons and the wood structure. Therefore the (visualisation) techniques used in this work could contribute. However, interdisciplinary research on wood chemistry, wood technology and wood biology, polymer technology, analytical methods, etc. is necessary. This interdisciplinary work is definitely a challenge to all involved scientists and can therefore lead to better insight and interesting results on the potential for additional (industrial) applications.

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Studies

1998-2003	Bio-Engineer in Land and Forest Management Thesis: "Houtkwaliteit en gebruiksmogelijkheden van inlands eiken en grenen uit de Kempen"
2003-2006	Postgraduate degree: "Doctoraatsopleiding in de Toegepaste Biologische Wetenschappen"

Work experience

09/03-12/06	PhD-student at the Laboratory of Wood Technology (FBE, UGent) EU-project "Improvement of Wood Product properties by increased hydrophobicity obtained by the use of silicon compounds", with as acronym HYDROPHOB (QLK5-CT-2002-01439).
01/07-08/07	PhD-student at the Laboratory of Wood Technology (FBE, UGent) EU-project "Furan and lignin based resins as eco-friendly and durable solutions for wood preservation, panel,

board and design products", with as acronym ECOBINDERS (NMP2-CT-2005-011734).

09/07-03/08 Scientific member at the Laboratory of Wood Technology (FBE, UGent)

04/08-present Assistant at the Department of Forest and Water Management (FBE, UGent)

Peer-reviewed publications (A1)

Printed or accepted for publication

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2004, Dynamiek van de aantasting van bomen door hout vretende zwammen, Doornik (B).

2004, Opleiding in praktische testen voor de bepaling van de toxiciteit van industriële effluenten en afvalstoffen, MicroBioTests Inc., Nazareth (B).

2006, COST E37 Sustainability through new technologies for enhanced wood durability. Workshop Durability classification of wooden materials in different commodities and use classes, London (UK).

2006, COST E37 Training Course Evaluation of field tests, Identification of microbial decay using light microscopy, Borås (S).

2008, HYDROPHOBE V, the Fifth International Conference on Water Repellent Treatment of Building Materials, Brussel (B)